Response Action Contract IX

QUALITY ASSURANCE PROJECT PLAN
OMEGA CHEMICAL SUPERFUND SITE OPERABLE UNIT 1
REMEDIAL INVESTIGATION/FEASIBILITY STUDY OVERSIGHT
ADDENDUM 01

MONTEBELLO FOREBAY
LOS ANGELES COUNTY, CALIFORNIA

U.S. Environmental Protection Agency
Contract No. 68-W-98-225

CH2M HILL, Inc.
and Team Subcontractors:
URS Group, Inc.
E2 Consulting Engineers, Inc.

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OMEGA CHEMICAL SUPERFUND SITE OPERABLE UNIT 1
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LOS ANGELES COUNTY, CALIFORNIA

EPA CONTRACT NO. 68-W-98-225
EPA WORK ASSIGNMENT NO. 174-RSBD-09BC
CH2M HILL PROJECT NO. 183120

Prepared for
U.S. Environmental Protection Agency
Region IX
75 Hawthorne Street
San Francisco, California 94105

Prepared by
CH2M HILL
Southern California Regional Office
3 Hutton Centre Drive, Suite 200
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April 2004

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CH2MHILL

April 9, 2004

183120

Christopher Lichens
U.S. EPA Region IX
Superfund Project Manager
75 Hawthorne Street
San Francisco, CA 94105

Subject: Sampling and Analysis Plan (FSP and QAPP) Addendum 01 for Omega Chemical Superfund Site Remedial Investigation/Feasibility Study Oversight

Dear Mr. Lichens:

Please find enclosed one copy of the subject documents for your review. If you have questions regarding the enclosed documents, please contact me at 909/890-9857.

Sincerely,

CH2M HILL

Tom Perina
Site Manager

Enclosures
c: David Taylor, U.S. EPA Region IX Quality Assurance Manager

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U.S. ENVIRONMENTAL PROTECTION AGENCY REGION IX

Plan Title:	Quality Assurance Project Plan Omega Chemical Superfund Site Remedial Investigation/Feasibility Study Oversight Addendum 01
Site Name:	Omega Chemical Superfund Site
Site Location:	Whittier
City/State/Zip:	Los Angeles County, California
Site EPA ID#:	09BC
Anticipated Sampling Dates:	2004
Prepared By:	Tom Perina
Date:	April 2004
Agency or Firm:	CH2M HILL, Inc.
Address:	164 West Hospitality Lane, Suite 2
City/State/Zip:	San Bernardino, California 92408
Telephone:	909/890-9857
EPA Work Assignment Manager:	Christopher Lichens Section: SFD-7-4
Phone No.	415/972-3149
QAPP Approval Date:	____________________

* *

Approved: Tom Perina, Ph.D., R.G., C.H.G. Tom Perina Date: April 2004
CH2M HILL Site Manager

Approved: Artemis Antipas, Ph.D. Artemis Antipas Date: April 2004
CH2M HILL Quality Assurance Officer

Approved: Christopher Lichens __________ Date: __________
EPA Work Assignment Manager

Approved: ____________________ Date: __________
EPA Quality Assurance Officer

* *

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_____ EPA Region IX Work Assignment Manager

_____ CH2M HILL Site Manager

_____ CH2M HILL Task Manager

_____ CH2M HILL Field Team Leader

_____ CH2M HILL Quality Assurance Manager

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Tables

Acronyms

AL	action level
AN	analytical support and data validation
AOC	administrative order on consent
ARAR	Applicable or Relevant and Appropriate Requirements
BOD	biological oxygen demand
CLP	contract laboratory program
COC	chain-of-custody
COD	chemical oxygen demand
Cr (VI)	hexavalent chromium
CRDL	contract-required detection levels
DE	data evaluation
DHS	Department of Health Services
DQO	data quality objective
EC	electrical conductivity
EE/CA	engineering evaluation/corrective action
EPA	Environmental Protection Agency
ERA	ecological risk assessment
FAR	Federal Acquisition Regulations
FSP	field sampling plan
GAC	granular activated carbon
GC	gas chromatography
GIS	geographic information system
HHRA	human health risk assessment
HSP	health and safety plan
ICP	inductively coupled plasma
ICP/MS	inductively coupled plasma/mass spectrometry
IMC	IMC Magnetics
LOE	level of effort

LUFT	Leaking Underground Fuel Tank
MAU	middle alluvial unit
MCL	maximum contaminant level
MDL	method detection limit
µg/L	micrograms per liter
mg/kg	milligrams per kilogram
MNA	monitored natural attenuation
MP	multiport
MS	matrix spike
MSD	matrix spike duplicate
msl	mean sea level
MTBE	methyl tertiary butyl ether
NDMA	n-nitrosodimethylamine
NPL	National Priorities List
OPOG	Omega Chemical Site PRP Organized Group
OU	operable unit
PCB	polychlorinated biphenyl
PCE	perchloroethylene (tetrachloroethene)
PHG	public health goal
POL	petroleum, oil, and lubricants
PRP	potentially responsible party
QA/QC	quality assurance/quality control
QAO	Quality Assurance Office
QAPP	quality assurance project plan
RA	remedial action
RAC	response action contract
RD	remedial design
RFA	request for analyses
RI/FS	remedial investigation/feasibility study
ROD	record of decision
RPD	relative percent difference
RPM	remedial project manager

RSCC	Regional Sample Control Center
RSD	relative standard deviation
RTL	review team leader
SM	site manager
SOW	statement of work
SRM	standard reference material
SSC	site safety coordinator
STL	sampling team leader
SVOC	semivolatile organic compound
TAL	Target Analyte List
1,1,1-TCA	1,1,1-trichloroethane
TCE	trichloroethylene (trichloroethene)
TCL	Target Compound List
TDS	total dissolved solids
TKN	total Kjeldahl nitrogen
TOC	total organic carbon
TPH	total petroleum hydrocarbons
TPHg	total petroleum hydrocarbons with gasoline distinction
TPHd	total petroleum hydrocarbons with diesel distinction
UAU	upper alluvial unit
VOC	volatile organic compound
VOH	Van Owen Holdings, LLC
WA	work assignment
WAM	work assignment manager

Introduction

This Quality Assurance Project Plan (QAPP) follows the United States Environmental Protection Agency (EPA) guidelines contained in *EPA Guidance for Quality Assurance Project Plans* (EPA, 1998), *EPA Requirements for Quality Assurance Project Plans* (EPA, March 2001). Thus, the following section headings correlate with the subtitles found in the EPA guidelines (EPA, December 2002).

This document is an Addendum to the QAPP issued in January 2004 (EPA, 2004a). This QAPP Addendum covers the additional sampling and analysis needed, due to recent disposal of waste oil in the Operable Unit 1 (OU-1) area by one of the tenants at the Omega site, as well as the addition of 1,4-dioxane analysis for the split sampling covered under the original QAPP.

Section A
Project Management/Data Quality Objectives

A.1 Project Organization

The same organization outlined in the original QAPP (EPA, 2004a) will apply.

A.2 Problem Definition/Background

A.2.1 Purpose

This QAPP Addendum presents the policies, organizations, objectives, and functional activities/procedures associated with the remedial investigation sampling and analysis activities at Omega Chemical Superfund Site and accompanies the data quality objectives (DQOs), which can be found in Appendix A (EPA, 1994 and 2000).

This QAPP Addendum follows EPA guidelines contained in *EPA Guidance for Quality Assurance Project Plans* (EPA, 1998 and 2002), and *EPA Requirements for Quality Assurance Project Plans* (EPA, 1999 and 2001). Thus, the following section headings correlate with the subtitles found in the EPA guidelines (EPA, 1998 and 2002).

A.2.2 Problem Statement

CH2M HILL has been conducting oversight of an ongoing Remedial Investigation/ Feasibility Study (RI/FS) conducted by Omega Chemical Site Potentially Responsible Party Organized Group (OPOG). The DQOs of this oversight RI/FS are provided in the original QAPP (EPA, 2004a).

It has been recently reported that Van Owen Holdings, LLC (VOH), one of the tenants at the Omega site, disposed of an unknown quantity of waste oil into a pit near groundwater monitoring well OW-1. EPA has responded and is requiring the tenant to conduct an investigation and cleanup of the contaminated soil at the site. As part of this investigation, CH2M HILL has been tasked with conducting split sampling of the contaminated soil, surrounding soil, and soil backfill material. One split sample will be collected from the contaminated soil, two split samples from the surrounding soil area (after excavation), and one split sample from the backfill material. Soil samples from each site will be analyzed for total petroleum hydrocarbons with gasoline and diesel distinction (TPHg and TPHd, respectively) volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), pesticides and polychlorinated biphenyls (PCBs), and metals. These analytes were selected to verify (1) that the oil-contaminated soil has been removed (TPHg and TPHd), and (2) that the spill has not impacted the ongoing investigation by introducing contaminants into the soil that are already known to be present at the site (VOCs, SVOCs, metals, pesticides, and PCBs).

This addendum also addresses additional 1,4-dioxane analysis for split soil and groundwater sampling during the ongoing OPOG RI/FS. The 1,4-dioxane results will provide additional contaminant characterization at the OU-1 site; 1,4-dioxane has been known to be present in groundwater at the site, but its source is yet unknown. The analysis for 1,4-dioxane has already been performed with provisional approval from EPA.

As related to the DQOs, CH2M HILL will perform oversight of VOH and OPOG as they perform the following activities:

- Collect soil samples from the oil spill site near monitoring well OW-1. These will include samples from contaminated or excavated soil, background/surrounding soil, and backfill material.
- Collect soil and groundwater samples for 1,4-dioxane analysis as part of the ongoing RI/FS by OPOG. These data are needed to update the past assessment of the nature and extent of VOC contamination at OU-1.

A.2.3 Background

Background information is provided in the original QAPP (EPA, 2004a).

A.2.4 Data Needs and Uses

Data needs and uses for the objectives described in this section have been identified through the DQO process presented in Appendix A. The data uses and needs are summarized in Tables A-1a (soil) and A-1b (groundwater) at the end of this section. Tables A-1a and A-1b list the analytes of concern and present regulatory criteria/action level requirements for organics and inorganics. These tables present a listing of applicable regulations and identify the lowest regulatory criteria where there are multiple regulatory criteria/action levels for a given analyte for the OPOG data. For this project, the criteria need to be at least as low as the OPOG data since the two sets will be compared. Thus, the OPOG regulatory limits were taken into consideration in selecting appropriate methods and laboratory reporting levels as described in Section A.4.2. Tables A-1a and A-1b list reporting limits, and Table A-2 lists the analytical methods selected to meet these criteria.

A.3 Project Description and Schedule

A.3.1 Description of Work to be Performed

A summary of the work to be performed relating to sample collection, analysis, and interpretation follows.

Field Investigation

CH2M HILL will conduct oversight of the oil spill investigation performed by the Omega tenant, VOH, near OW-1 and the ongoing OPOG RI/FS field investigation at OU-1. CH2M HILL will collect split environmental samples and information required in support of the oversight.

Sample Analysis

CH2M HILL will arrange for a contract laboratory program (CLP) type sample analysis of split environmental samples collected during the tasks described in this QAPP Addendum.

Analytical Support and Data Validation

CH2M HILL will perform the validation of the split samples to ensure that adequate and definable sample management and techniques are implemented.

Data Evaluation

CH2M HILL will organize and evaluate data gathered during the tasks. The data evaluation activities will include:

- Data usability evaluation and field quality assurance/quality control (QA/QC)
- Data reduction, tabulation, and evaluation

A.3.2 Schedule of Activities

The oil spill investigation is anticipated to take place in April 2004. The duration of the investigation is at the discretion of the Omega tenant.

The OU-1 RI/FS investigation is currently ongoing and will continue at the discretion of OPOG.

A.4 Data Quality Objectives

A.4.1 Project Quality Objectives

The specific needs for data that will be collected during each activity were examined to evaluate whether project objectives for the RI are optimally achieved. Specific DQOs were considered independently through the DQO process (EPA Q4/G4 [EPA, 1994 and 2000]) to meet the needs of the data user for each activity. Appendix A presents the DQO decisionmaking process for the remedial field activities.

A.4.2 Measurement Performance Criteria

The QA objective of this plan is to develop implementation procedures that will provide data of known and appropriate quality for the needs identified in previous sections. Data quality is assessed by representativeness, comparability, accuracy, precision, and completeness. These terms, the applicable procedures, and level of effort are described below.

The applicable QC procedures, quantitative target limits, and level of effort for assessing data quality are dictated by the intended use of the data and the nature of the analytical methods. Analytical parameters and applicable detection levels, analytical precision, accuracy, and completeness in alignment with needs identified in Section A-2.4 are presented in Table A-2.

Reporting detection limits/target detection limits (Tables A-1a, A-1b, and A-2) are per-method reporting limits, equivalent to contract-required detection limits (CRDLs). "Target" implies that final sample detection limits may be higher because of sample matrix effects. Detection limits for the individual samples will be reported in the final data.

Laboratory-specific method detection limits (MDLs) are significantly below reporting limits. Where reporting limits are higher than regulatory limits, the project team will use MDLs as needed for project decisions. This is not expected to impact project decisions.

Representativeness is a measure of how closely the results reflect the actual concentration or distribution of the chemical compounds in the matrix samples. Sampling plan design, sampling techniques, and sample-handling protocols (e.g., for storage, preservation, and transportation) have been developed, and are discussed in subsequent sections of this document. The proposed documentation will establish that protocols have been followed and sample identification and integrity ensured.

Comparability expresses the confidence with which one data set can be compared to another. Data comparability will be maintained using defined procedures and the use of consistent methods and consistent units. Actual detection limits will depend on the sample matrix and will be reported as defined for the specific samples.

Accuracy is an assessment of the closeness of the measured value to the true value. For samples, accuracy of chemical test results is assessed by spiking samples with known standards and establishing the average recovery. For a matrix spike, known amounts of a standard compound identical to the compounds being measured are added to the sample. A quantitative definition of average recovery accuracy is given in Section D.3. The level of effort (LOE) for accuracy measurements will be a minimum frequency of 1 in 20 samples analyzed.

Precision is a measure of the data spread when more than one measurement has been collected from the same sample. Precision can be expressed as the relative percent difference; a quantitative definition is given in Section D.3. The level of effort (LOE) for precision measurements will be a minimum of 1 in 20 samples analyzed.

Completeness is a measure of the amount of valid data obtained from the analytical measurement system and the complete implementation of defined field procedures. The quantitative definition of completeness is given in Section D.3. The target completeness objective will be 90 percent; the actual completeness may vary depending on the intrinsic nature of the samples. The completeness of the data will be assessed during QC reviews.

A.5 Special Training Requirements/Certification (A8)

All project staff working on the site will be health and safety trained, and will follow requirements specified in the Health and Safety Plan (HSP) for the project, which can be found in the companion Field Sampling Plan (FSP) (EPA, 2004b). The HSP describes the specialized training required for personnel on this project and the documentation and tracking of this training.

A.6 Documentation and Records

Field documentation and records will be as described in Section B and the FSP. Laboratory documentation will be per: (1) methods and quality assurance protocols listed in Section B, and (2) EPA Regional Laboratory specific standard operating procedures. Overall project documentation will be per the EPA Region IX Response Action Contract (RAC) Program Plan.

TABLE A-1a
Data Needs and Uses – Soil

Parameter	Data Use	Regulatory Limit/ Action Level (mg/kg)[1]	Laboratory Target Reporting Limit (mg/kg)[2]
SOIL			
California Assessment Manual (CAM) Metals			
Antimony	Comparison to Tenant data	31	10.0
Arsenic – Method 6020	Comparison to Tenant data	0.39	0.5
Barium	Comparison to Tenant data	5,375	1.0
Beryllium	Comparison to Tenant data	154	1.0
Cadmium	Comparison to Tenant data	37	0.50
Chromium	Comparison to Tenant data	100,000	20
Cobalt	Comparison to Tenant data	4,692	10.0
Copper	Comparison to Tenant data	2,905	2.0
Lead	Comparison to Tenant data	400	10.0
Mercury – Method 7471A	Comparison to Tenant data	23	0.10
Molybdenum	Comparison to Tenant data	391	3.0
Nickel	Comparison to Tenant data	1,564	2.0
Selenium	Comparison to Tenant data	391	3.0
Silver	Comparison to Tenant data	391	1.0
Thallium	Comparison to Tenant data	5.2	6.0
Vanadium	Comparison to Tenant data	547	1.0
Zinc	Comparison to Tenant data	23,463	1.0
Volatile Organic Compounds (VOCs)			
Acetone	Comparison to Tenant data	1,444	0.010
Benzene	Comparison to Tenant data	0.62	0.002
Bromobenzene	Comparison to Tenant data	28.1	0.005
Bromochloromethane	Comparison to Tenant data	—	0.0005
Bromodichloromethane	Comparison to Tenant data	0.98	0.002
Bromoform	Comparison to Tenant data	56.2	0.005
Bromomethane	Comparison to Tenant data	3.84	0.005
n-Butylbenzene	Comparison to Tenant data	134	0.005
sec-Butylbenzene	Comparison to Tenant data	105	0.005
tert-Butylbenzene	Comparison to Tenant data	122	0.005
Carbon tetrachloride	Comparison to Tenant data	0.23	0.005
Chlorobenzene	Comparison to Tenant data	53.8	0.002
Chloroethane	Comparison to Tenant data	1,600	0.005
Chloroform	Comparison to Tenant data	0.24	0.002
Chloromethane	Comparison to Tenant data	1.21	0.005
2-Chlorotoluene	Comparison to Tenant data	152	0.005
4-Chlorotoluene	Comparison to Tenant data	—	0.005
Dibromochloromethane	Comparison to Tenant data	5.28	0.002
1,2-Dibromo-3-chloropropane	Comparison to Tenant data	0.32	0.005

TABLE A-1a
Data Needs and Uses – Soil

Parameter	Data Use	Regulatory Limit/ Action Level (mg/kg)[1]	Laboratory Target Reporting Limit (mg/kg)[2]
1,2-Dibromoethane	Comparison to Tenant data	0.0049	0.002
Dibromomethane	Comparison to Tenant data	545	0.002
1,2-Dichlorobenzene	Comparison to Tenant data	370	0.002
1,3-Dichlorobenzene	Comparison to Tenant data	40.6	0.002
1,4-Dichlorobenzene	Comparison to Tenant data	3.03	0.002
Dichlorodifluoromethane (Freon 12)	Comparison to Tenant data	93.6	0.005
1,1-Dichloroethane	Comparison to Tenant data	571	0.002
1,2-Dichloroethane	Comparison to Tenant data	0.34	0.002
1,1-Dichloroethene	Comparison to Tenant data	0.052	0.005
cis-1,2-Dichloroethene	Comparison to Tenant data	41.9	0.002
trans-1,2-Dichloroethene	Comparison to Tenant data	62.1	0.002
1,2-Dichloropropane	Comparison to Tenant data	0.34	0.002
1,3-Dichloropropane	Comparison to Tenant data	—	0.002
2,2-Dichloropropane	Comparison to Tenant data	—	0.002
1,1-Dichloropropene	Comparison to Tenant data	—	0.002
cis-1,3-Dichloropropene	Comparison to Tenant data	0.081	0.002
trans-1,3-Dichloropropene	Comparison to Tenant data	0.081	0.002
Ethylbenzene	Comparison to Tenant data	230	0.002
Hexachlorobutadiene	Comparison to Tenant data	5.69	0.005
Isopropylbenzene	Comparison to Tenant data	156	0.002
p-Isopropyltoluene	Comparison to Tenant data	—	0.002
Methylene chloride	Comparison to Tenant data	8.49	0.020
Methyl tert-butyl ether	Comparison to Tenant data	—	0.005
Naphthalene	Comparison to Tenant data	54.8	0.005
n-Propylbenzene	Comparison to Tenant data	134	0.002
Styrene	Comparison to Tenant data	1,700	0.002
1,1,1,2-Tetrachloroethane	Comparison to Tenant data	2.85	0.005
1,1,2,2-Tetrachloroethane	Comparison to Tenant data	0.36	0.002
Tetrachloroethene	Comparison to Tenant data	4.72	0.002
Toluene	Comparison to Tenant data	520	0.002
1,2,3-Trichlorobenzene	Comparison to Tenant data	—	0.005
1,2,4-Trichlorobenzene	Comparison to Tenant data	475	0.005
1,1,1-Trichloroethane	Comparison to Tenant data	685	0.002
1,1,2-Trichloroethane	Comparison to Tenant data	0.815	0.002
Trichloroethene	Comparison to Tenant data	2.71	0.002
Trichlorofluoromethane (Freon 11)	Comparison to Tenant data	383	0.005
1,2,3-Trichloropropane	Comparison to Tenant data	0.0014	0.010

TABLE A-1a
Data Needs and Uses – Soil

Parameter	Data Use	Regulatory Limit/ Action Level (mg/kg)[1]	Laboratory Target Reporting Limit (mg/kg)[2]
Trichlorotrifluoroethane (Freon 113)	Comparison to Tenant data	5,600	0.005
1,2,4-Trimethylbenzene	Comparison to Tenant data	51.3	0.002
1,3,5-Trimethylbenzene	Comparison to Tenant data	21.2	0.002
Vinyl chloride	Comparison to Tenant data	0.021	0.005
o-Xylene	Comparison to Tenant data	210	0.002
m,p-Xylenes	Comparison to Tenant data	280	0.002
Semivolatile Organic Compounds (SVOCs)			
Base/Neutral Extractables			
1,2,4-Trichlorobenzene	Comparison to Tenant data	646	0.7
1,2-Dichlorobenzene	Comparison to Tenant data	370	0.7
1,3-Dichlorobenzene	Comparison to Tenant data	13	0.7
1,4-Dichlorobenzene	Comparison to Tenant data	3.4	0.7
2,4-Dinitrotoluene	Comparison to Tenant data	0.71	0.7
2,6-Dinitrotoluene	Comparison to Tenant data	0.71	0.7
2-Chloronaphthalene	Comparison to Tenant data	3,852	0.7
2-Methylnaphthalene	Comparison to Tenant data	—	0.7
2-Nitroaniline	Comparison to Tenant data	3.5	3.3
3-Nitroaniline	Comparison to Tenant data	—	3.3
3,3'-Dichlorobenzidine	Comparison to Tenant data	1.1	1.3
4-Bromophenyl phenyl ether	Comparison to Tenant data	—	0.7
4-Chloroaniline	Comparison to Tenant data	244	1.3
4-Chlorophenyl phenyl ether	Comparison to Tenant data	—	0.7
4-Nitroaniline	Comparison to Tenant data	—	3.3
Acenaphthylene	Comparison to Tenant data	3,681	0.7
Acenaphthene	Comparison to Tenant data	3,681	0.7
Anthracene	Comparison to Tenant data	21,896	0.7
Benz(a)anthracene	Comparison to Tenant data	0.62	0.7
Benzo(a)pyrene	Comparison to Tenant data	0.062	0.7
Benzo(b)fluoranthene	Comparison to Tenant data	0.62	0.7
Benzo(g,h,I)perylene	Comparison to Tenant data	—	0.7
Benzl alcohol	Comparison to Tenant data	18,330	1.3
Bis(2-chloroethoxy)methane	Comparison to Tenant data	—	0.7
Bis(2-chloroethyl)ether	Comparison to Tenant data	0.21	0.7
Bis(2-chloroisopropyl)ether	Comparison to Tenant data	2.9	0.7
Bis(2-ethylhexyl)phthalate	Comparison to Tenant data	35	0.7
Butyl benzylphthalate	Comparison to Tenant data	12,220	0.7
Chrysene	Comparison to Tenant data	62	0.7
Di-n-butylphthalate	Comparison to Tenant data	6,110	0.7

TABLE A-1a
Data Needs and Uses – Soil

Parameter	Data Use	Regulatory Limit/ Action Level (mg/kg)[1]	Laboratory Target Reporting Limit (mg/kg)[2]
Di-n-octylphthalate	Comparison to Tenant data	1,222	0.7
Dibenz(a,h)anthracene	Comparison to Tenant data	0.062	0.7
Dibenzofuran	Comparison to Tenant data	290	0.7
Diethyl phthalate	Comparison to Tenant data	48,882	0.7
Dimethyl phthalate	Comparison to Tenant data	100,000	0.7
Fluoranthene	Comparison to Tenant data	2,293	0.7
Fluorene	Comparison to Tenant data	2,643	0.7
Hexachlorobenzene	Comparison to Tenant data	0.30	0.7
Hexachlorobutadiene	Comparison to Tenant data	6.2	0.7
Hexachlorocyclopentadiene	Comparison to Tenant data	423	0.7
Hexachloroethane	Comparison to Tenant data	35	0.7
Indeno(1,2,3-cd)pyrene	Comparison to Tenant data	0.62	0.7
Isophorone	Comparison to Tenant data	511	0.7
n-Nitrosodiphenylamine	Comparison to Tenant data	99	0.7
n-Nitrosodi-n-propylamine	Comparison to Tenant data	0.069	0.7
Naphthalene	Comparison to Tenant data	56	0.7
Nitrobenzene	Comparison to Tenant data	20	0.7
Phenanthrene	Comparison to Tenant data	—	0.7
Pyrene	Comparison to Tenant data	2,308	0.7
SVOCs: Acid Extractables			
2,4,5-Trichlorophenol	Comparison to Tenant data	6,110	3.3
2,4,6-Trichlorophenol	Comparison to Tenant data	44	0.3
2,4-Dichlorophenol	Comparison to Tenant data	183	0.3
2,4-Dimethylphenol	Comparison to Tenant data	1,222	0.3
2,4-Dinitrophenol	Comparison to Tenant data	122	3.3
2-Chlorophenol	Comparison to Tenant data	63	0.3
2-Methylphenol	Comparison to Tenant data	3,055	0.3
2-Nitrophenol	Comparison to Tenant data	—	0.3
4,6-Dinitro-2-methylphenol	Comparison to Tenant data	—	3.3
4-Chloro-3-methylphenol	Comparison to Tenant data	—	1.3
4-Methylphenol	Comparison to Tenant data	305	0.3
4-Nitrophenol	Comparison to Tenant data	488	1.6
Benzoic Acid	Comparison to Tenant data	100,000	1.6
Pentachlorophenol	Comparison to Tenant data	3.0	3.3
Phenol	Comparison to Tenant data	36,661	0.3

TABLE A-1a
Data Needs and Uses – Soil

Parameter	Data Use	Regulatory Limit/ Action Level (mg/kg)[1]	Laboratory Target Reporting Limit (mg/kg)[2]
Pesticides and Polychlorinated Biphenyls (PCBs)			
Organochlorine Pesticides – 8081A			
α-BHC	Comparison to Tenant data	0.09	0.019
β-BHC	Comparison to Tenant data	0.32	0.033
δ-BHC	Comparison to Tenant data	—	0.011
γ-BHC (Lindane)	Comparison to Tenant data	0.44	0.020
α-Chlordane	Comparison to Tenant data	1.6	0.015
γ-Chlordane	Comparison to Tenant data	1.6	0.015
4,4'-DDD	Comparison to Tenant data	2.4	0.042
4,4'-DDE	Comparison to Tenant data	1.7	0.025
4,4'-DDT	Comparison to Tenant data	1.7	0.036
Aldrin	Comparison to Tenant data	0.029	0.022
Dieldrin	Comparison to Tenant data	0.03	0.035
Endosulfan I	Comparison to Tenant data	366	0.021
Endosulfan II	Comparison to Tenant data	366	0.024
Endosulfan Sulfate	Comparison to Tenant data	—	0.036
Endrin	Comparison to Tenant data	18	0.036
Endrin Aldehyde	Comparison to Tenant data	—	0.016
Heptachlor	Comparison to Tenant data	0.11	0.020
Heptachlor Epoxide	Comparison to Tenant data	0.053	0.021
Methoxychlor	Comparison to Tenant data	305	0.057
Toxaphene	Comparison to Tenant data	0.44	0.57
PCBs – 8082			
PCB-1016	Comparison to Tenant data	3.9	0.70
PCB-1221	Comparison to Tenant data	0.22	0.70
PCB-1232	Comparison to Tenant data	0.22	0.70
PCB-1242	Comparison to Tenant data	0.22	0.70
PCB-1248	Comparison to Tenant data	0.22	0.70
PCB-1254	Comparison to Tenant data	0.22	0.70
PCB-1260	Comparison to Tenant data	0.22	0.70
Emergent Compounds			
1,4-dioxane	Comparison to OPOG data	44	1 ppm

TABLE A-1a
Data Uses and Needs – Soils

Other Compounds			
Parameter	**Data Use**	**Regulatory Limit/ Action Level (ppm)[3]**	**Laboratory Target Reporting Limit (ppm)**
Total Petroleum Hydrocarbons – Gasoline	Comparison to Tenant data	10	5
Total Petroleum Hydrocarbons – Diesel	Comparison to Tenant data	100	20
Total Petroleum Hydrocarbons – Heavy oil	Comparison to Tenant data	–	20

Notes:
[1]EPA Region IX Preliminary Remediation Goals (PRGs) for residential soils.
[2]Reporting Limits (RLs) shown are for samples that have not been diluted. RLs are matrix dependent and may be higher or lower than listed.
[3]Leaching potential analysis for gasoline and diesel using total petroleum hydrocarbons (TPH) and benzene, toluene, ethylbenzene, and xylene (BTEX), Leaking Underground Fuel Tank (LUFT) Field Manual: Guidelines for Site Assessment, Cleanup, and Underground Storage Tank Closure (October, 1989).
– No Standard

TABLE A-1b
Data Needs and Uses– Groundwater

Emergent Compounds			
Parameter	**Data Use**	**Regulatory Limit/ Action Level (µg/L)[1]**	**Laboratory Target Reporting Limit (µg/L)[2]**
GROUNDWATER			
1,4-Dioxane	Comparison to OPOG data	3	2

Notes:
[1] California Department of Health Services state action level for toxicity.
[2]Reporting Limits (RLs) shown are for samples that have not been diluted. RLs are matrix dependent and may be higher or lower than listed.

TABLE A-2
Measurement Performance Criteria
Omega Chemical Superfund Site, California

Parameter [a]	Method [b]	Reporting Limit/Target Detection Limit (µg/L)	Analytical Accuracy (% Recovery)	Analytical Precision (Relative % Deviation)	Overall Completeness (%)
Soil:					
Volatile Organics [a]	CLP [b]	c	CLP	CLP	90
Semivolatile Organics [a]	CLP	c	CLP	CLP	90
Pesticides and polychlorinated biphenyls [a]	CLP	c	CLP	CLP	90
Metals[a]	CLP	c	CLP	CLP	90
TPH (Gasoline, Diesel, Heavy Oil	8015 Mod [d]	C	50-150	±50	90
Water:					
1,4-Dioxane	8270 [d]	C	50-150	±50	90

[a]Target analytes per Tables A-1a and A-1b.

[b]Contract Laboratory Program (CLP) method per EPA Contract Laboratory Statement of Work.

The analyses for volatiles, semivolatiles, pesticides/polychlorinated biphenyls, and metals will be per EPA CLP methodology and laboratories. Since the required detection limits and the analyte lists differ from the standard CLP lists, the analyses will be carried out per special services provisions currently available under the CLP. Low-level ICP/MS statement of work (ILM 5.1) will be used for metals. Similarly, the low-level organic statement of work (OLC 3.2) or larger sample volumes may be used to attain lower-level organic detection limits. If CLP is unavailable, the analyses can be carried out at the EPA Regional Laboratory using the standard operating procedures of the laboratory and QA equivalent to CLP.

[c]Required detection limits are listed in Tables A-1a and A-1b.

[d]EPA Regional Laboratory Standard Operating Procedures are provided in Appendix B.

Section B
Measurement Data Acquisition

This section presents sampling process design and requirements for sampling methods, sample handling and custody, analytical methods, QC, and instrumentation for the sampling activities that will be conducted as a part of the RI/FS at the Omega Chemical Superfund site. Data acquisition requirements and data management for these sampling events are also addressed in this section.

B.1 Sampling Process Design

The sampling process and design for the oil spill is provided in Step 7 of the DQOs in Appendix A. The sampling locations and number of samples are shown in the associated FSP.

For 1,4-dioxane split sample analyses, the sampling will be the same as outlined in the original QAPP (EPA, 2004a).

B.2 Sampling Method Requirements

Sampling method requirements have been detailed in the associated FSP in Section 5.

B.3 Sample Handling and Custody Requirements

Sample handling and custody requirements will be the same as outlined in the original QAPP (EPA, 2004a).

B.4 Analytical Method Requirements

Project analytes, methods, and required detection limits are listed in Table A-2.

The soil analyses for volatiles, semivolatiles, pesticides/PCBs and metals will be per EPA CLP methodology and laboratories. Since the required detection limits and the analyte lists differ from the standard CLP lists, the analyses will be carried out per special services provisions currently available under the CLP. The low-level inductively coupled plasma/mass spectrometry (ICP/MS) statement of work (ILM 5.1) will be used for metals. Similarly, the low-level organic statement of work (OLC 3.2) or larger sample volumes may be used to attain lower- level organic detection limits. Samples for VOCs in soil will be collected and preserved following EPA Method 5035 by the OPOG for both splits. If CLP is unavailable, the analyses can be carried out at the EPA Regional Laboratory using the standard operating procedures of the laboratory and QA equivalent to CLP.

TPH analyses for gasoline, diesel, and heavy oil fractions will be per EPA Method 8015 (modified per California State [LUFT] methodology) and the Regional Laboratory specifications shown in Appendix B.

For 1,4-dioxane, analyses will be per EPA Method 8270 per the Regional Laboratory Standard Operating Procedure provided in Appendix B.

B.5 Quality Control Requirements

B.5.1 Field QC Procedures

QC requirements related to the sample collection process (i.e., design, methods, handling, and custody) requirements have been discussed in the previous sections of this document.

Field QC samples include field duplicates, field blanks, and laboratory QC samples (for matrix spike/matrix spike duplicates [MS/MSDs]). QC samples will be collected immediately following collection of target samples, using the same procedures as used for the collection of the target sample. These procedures are presented in the FSP. Field blank samples are not needed for the split samples as the sampling will be carried out by the OPOG. Trip blanks will be included with the split, oversight volatile organics samples. Since OPOG will be collecting the samples, field blanks will be included with the OPOG samples. Some LOE will be implemented for the oil spill sampling.

B.5.2 Laboratory Procedures

Laboratory QC procedures will include the following:

- Analytical methodology according to specific methods listed in Table A-2 and Appendix B.
- Instrument calibrations and standards as defined in specific methods listed in the CLP statement of work and Appendix B.
- Laboratory blank measurements per CLP statement of work and Appendix B.
- Accuracy and precision measurements per CLP statement of work., at a minimum of 1 in 20, 1 per batch and Appendix B.
- Data reduction and reporting according to specific methods listed in Table A-2.
- Laboratory documentation equivalent to the CLP statement of work.

B.6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements

Instrument and equipment testing, inspection, and maintenance requirements will be the same as outlined in the original QAPP (EPA, 2004a).

B.7 Instrument Calibration and Frequency

Instrument calibration and frequency will be the same as outlined in the original QAPP (EPA, 2004a).

B.8 Data Acquisition Requirements (Nondirect Measurements)

Previously collected data and other information will be used to assist decisionmaking during the RI/FS. These data will be in both hard copy and electronic format. Electronic data will be handled by the electronic data management system described below.

B.9 Data Management

All data for all parameters will undergo two levels of review and validation: (1) at the laboratory, and (2) outside the laboratory as described in Section D. After the validated data are received, they will be input into the project database to facilitate database inquires and report preparation. The data will be stored in the databases with all laboratory qualifiers included. Established data queries and formats developed during the previous work assignments (WAs) will be adapted for incorporation of laboratory data from ASCII files, provided by the EPA Quality Assurance Office (QAO), to files compatible with the project database. The database will be maintained in a manner that is compatible with, and provided to, EPA, or others, at the request of EPA. Major components for complete data management will be as follows:

- **Data Conversion/Manipulation/Review.** Reports of data from sampling are received from the QAO in hardcopy or electronic format. These data must be converted, input, reviewed, and QC checked.

  In addition, available data from other sources may be incorporated into the database. These data will need to be manually input, output, reviewed, QC checked, then uploaded into the database.

- **Preparation of Tables.** Data tables will be prepared following receipt of validated data from the QAO following each sample event of the WA. Queries will be created for the database to generate updated tables.

- **Database Documentation.** An update of the database and complete documentation will be performed at the end of the project. The commands, file names, and general operating procedures for all the data queries will be documented as directed by the EPA work assignment manager (WAM). This documentation will be provided to EPA and transferred to others (at the request of EPA).

Section C
Assessment/Oversight

C.1 Assessment and Response Actions

The review team and the site manager (SM) will monitor the performance of the QA procedures. If problems arise and the WAM directs the SM, the review team will conduct field audits, currently not scheduled or included in the statement of work (SOW). Audits may be scheduled to evaluate (1) the execution of sample identification, chain-of-custody (COC) procedures, field notebooks, sampling procedures, and field measurements; (2) whether trained personnel staffed the sample event; (3) whether equipment was in proper working order (i.e., calibration); (4) the availability of proper sampling equipment; (5) whether appropriate sample containers, sample preservatives, and techniques were used; (6) whether sample packaging and shipment were appropriate; and (7) whether QC samples were properly collected.

The analyses are expected to be performed by the EPA CLP laboratories and/or the EPA Regional Laboratory. The distribution of analyses may change at the time of analysis depending on availability. The QA of the of the CLP is centrally managed by EPA. The QA of the Regional Laboratory is managed by the EPA QAO. Laboratories subcontracted to CH2M HILL, if any, will be selected based on prior performance on Regional Superfund projects. Additionally, onsite audits or performance evaluation samples will be administered by the project QAO, as necessary.

Audits will be followed up with an audit report prepared by the reviewer. The auditor will also debrief the laboratory or the field team at the end of the audit and request that the laboratory or field team comply with the corrective action request.

C.1.1 Reporting and Resolution of Issues

If QC audits result in detection of unacceptable conditions or data, the SM will be responsible for developing and initiating corrective action. The WAM will be notified if nonconformance is of program significance or requires special expertise not normally available to the project team. In such cases, the remedial project manager (RPM) will decide whether any corrective action should be pursued. Corrective action may include the following:

- Reanalyzing samples if holding time criteria permit
- Resampling and analyzing
- Evaluating and amending sampling and analytical procedures
- Accepting data acknowledging a level of uncertainty

C.2 Reports to Management

The SM or WAM may request that a QA report be made to the WAM on the performance of sample collection and data quality. The report will include the following:

- Assessment of measurement data accuracy, precision, and completeness
- Results of performance audits
- Results of systems audits
- Significant QA problems and recommended solutions

Monthly progress reports will summarize overall project activities and any problems encountered. QA reports generated on sample collection and data quality will focus on specific problems encountered and solutions implemented. Alternatively, in lieu of a separate QA report, sampling and field measurement data quality information may be summarized and included in the final reports summarizing field activities (e.g., well installation or aquifer testing technical memoranda). The objectives, activities performed, overall results, sampling, and field measurement data quality information of the project will be summarized and included in the final field activity reports along with any QA reports.

Section D
Data Validation and Usability

D.1 Data Review, Validation, and Verification Requirements

All data for all parameters will undergo two levels of review and validation: (1) at the laboratory, and (2) outside the laboratory by the EPA Quality Assurance Management Section or their designee. One hundred percent of data will be reviewed outside the laboratory at EPA Region IX Tier 3 LOE. This LOE is based on the lower number of samples (only one analytical batch for each method is expected). Because the data will be used to evaluate/validate OPOG data, a comprehensive review is needed.

D.2 Validation and Verification Methods

Initial data reduction, validation, and reporting at the laboratory will be performed as described in the laboratory standard operating procedures.

Independent data validation by EPA or their designee will follow EPA *Contract Laboratory Program National Functional Guidelines for Inorganic/Organic Data Review* (EPA, 1994 and 1999, 2001, 2002) as described above.

The following guidelines may be used in comparing the EPA and the OPOG data:

Guidance for Comparing Split Sample Data

Matrix	Parameter	Disagreement	Major Disagreement
All	All	>5x difference when one result is <DL	>10x difference when one result is <DL
All	All	>3x difference when one result is <RL	>5x difference when one result is <RL
Water	All except POL	>2x difference	>3x difference
Soil	All except Metals, VOCs, BTEX, POL	>4x difference	>5x difference
Soil	Metals	>2x difference	>3x difference
Water & Soil	POL	>3x difference	>5x difference
Soil	VOC, BTEX	>5x difference	>10x difference

<DL: less than estimated method detection limit (i.e., "ND").
<RL: less than Reporting Limit (i.e., "J"-flagged).
Petroleum, oil, and lubricants (POL): chromatographic fuel-range analyses (e.g., 8015 Methods)

In case of a major disagreement, sampling and analytical data will be reviewed to establish the cause of discrepancy first. Subsequently, the deviation will be discussed with OPOG for relevant corrective actions (resampling, reanalysis, etc.) or explanation/data qualification as appropriate.

D.3 Reconciliation with Data Quality Objectives

Results obtained from the project will be reconciled with the requirements specified in Table A-2 of this QAPP. Assessment of data for precision, accuracy, and completeness will be per the following quantitative definitions.

D.3.1 Precision

If calculated from duplicate measurements:

$$RPD = \frac{(C_1 - C_2) \times 100\%}{(C_1 + C_2) / 2}$$

RPD = relative percent difference
C_1 = larger of the two observed values
C_2 = smaller of the two observed values

If calculated from three or more replicates, use relative standard (RSD) rather than relative percent difference (RPD):

$$RSD = (s / \bar{y}) \times 100\%$$

RSD = relative standard deviation
s = standard deviation
$\bar{y}$ = mean of replicate analyses

Standard deviation, s, is defined as follows:

$$S = \sqrt{\sum_{i=1}^{n} \frac{(y_i / y)^{-2}}{n-1}}$$

s = standard deviation
y_i = measured value of the i^{th} replicate
$\bar{y}$ = mean of replicate analyses
n = number of replicates

D.3.2 Accuracy

For measurements where matrix spikes are used:

$$\%R = 100\% \times \left[\frac{S - U}{C_{sa}} \right]$$

%R = percent recovery
S = measured concentration in spiked aliquot
U = measured concentration in unspiked aliquot
C_{sa} = actual concentration of spike added

For situations where a standard reference material (SRM) is used instead of, or in addition to, matrix spikes:

$$\%R = 100\% \times \left[\frac{C_m}{C_{sm}}\right]$$

%R = percent recovery
C_m = measured concentration of SRM
C_{sm} = actual concentration of SRM

D.3.3 Completeness (Statistical)

Defined as follows for all measurements:

$$\%C = 100\% \times \left[\frac{V}{T}\right]$$

%C = percent completeness
V = number of measurements judged valid
T = total number of measurements

References

Camp Dresser and McKee. 2003. Final On-Site Soils Remedial Investigation/Feasibility Study Work Plan. September 29.

U.S. Environmental Protection Agency (EPA). 1998 and 2002. *EPA Guidance for Quality Assurance Project Plans*. EPA QA/G5, EPA/240/R-02/009.

U.S. Environmental Protection Agency (EPA). 1994 and 2000. *Guidance for the Data Quality Objectives Process*. EPA QA/G4.

U.S. Environmental Protection Agency (EPA). 1994, 1999, 2001 and 2002. *Contract Laboratory Program National Functional Guidelines for Inorganic/ Organic Data Review.*

U.S. Environmental Protection Agency (EPA). 1999 and 2001. *EPA Requirements for Quality Assurance Project Plans* (QA/R-5) - March 2001, EPA/240/B-01/003.

U.S. Environmental Protection Agency (EPA). 2004a. *Quality Assurance Project Plan, Omega Chemical Superfund Site, Remedial Investigation/Feasibility Study Oversight*. Prepared by CH2M HILL. January.

U.S. Environmental Protection Agency (EPA). 2004b. *Field Sampling Plan, Omega Chemical Superfund Site, Remedial Investigation/Feasibility Study Oversight*. Prepared by CH2M HILL. January.

Appendix A
Data Quality Objectives

Appendix A
Data Quality Objectives
Remedial Investigation/Feasibility Study Oversight
Omega Chemical Superfund Site Operable Unit 1 (OU-1)
Addendum 01

Step 1. State the Problem

(1) *Identify members of the planning team* – The members of the planning team are the Environmental Protection Agency (EPA) Work Assignment Manager (WAM), CH2M HILL Site Manager (SM), CH2M HILL hydrogeologists, and CH2M HILL Quality Assurance Officer (QAO).

(2) *Identify the primary decisionmaker* – There will not be a primary decisionmaker. Decisions will be made by consensus.

Develop a concise description of the problem – CH2M HILL has been conducting oversight of an ongoing Remedial Investigation/Feasibility Study (RI/FS) conducted by the Omega Chemical Site Potentially Responsible Party Organized Group (OPOG). The data quality objectives (DQOs) of this oversight RI/FS are provided in the original Quality Assurance Project Plan (QAPP), submitted to the EPA in January 2004 (EPA, 2004a).

It has been recently reported that one of the tenants at the Omega site illegally disposed of an unknown quantity of waste oil into a pit near groundwater monitoring well OW-1. EPA has responded and is requiring the tenant to conduct an investigation and cleanup of the contaminated soil at the site. As part of this investigation, CH2M HILL has been tasked with conducting split sampling of the contaminated soil, surrounding soil, and soil backfill material. One split sample will be collected from the contaminated soil, two split samples from the surrounding soil area (after excavation), and one split sample from the backfill material. Soil samples from each site will be analyzed for total petroleum hydrocarbons with gasoline and diesel distinction (TPHg and TPHd, respectively) volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), pesticides and polychlorinated biphenyls (PCBs), and metals. These analytes were selected to verify (1) that the oil-contaminated soil has been removed (TPHg and TPHd), and (2) that the spill has not impacted the ongoing investigation by introducing into the soil contaminants that are already known to be present at the site (VOCs, SVOCs, metals, pesticides, and PCBs).

This addendum also addresses additional split soil and groundwater sampling for 1,4-dioxane analysis during the ongoing RI/FS by OPOG. The 1,4-dioxane results will provide additional contaminant characterization at the OU-1 site; 1,4-dioxane has been known to be present in groundwater at the site, but its source is yet unknown. The analysis for 1,4-dioxane has already been performed with provisional approval from EPA.

As related to the DQOs, the CH2M HILL will perform oversight of the Omega tenant and OPOG including:

(a) Collection of split samples from the oil spill site near monitoring well OW-1. These include samples from contaminated or excavated soil, background/surrounding soil, and backfill material.

(b) Collection of split soil and groundwater samples for 1,4-dioxane analysis as part of oversight of the OPOG ongoing RI/FS. These data are needed to update the past assessment of the nature and extent of VOC contamination at OU-1.

A summary of the work to be performed relating to sample collection, analysis, and interpretation follows.

Field Investigation (FI)
CH2M HILL will conduct oversight of the oil spill investigation performed by the Omega tenant near OW-1 and the OPOG ongoing RI/FS field investigation at OU-1. CH2M HILL will collect split environmental samples and information required in support of the oversight.

Sample Analysis (SN)
CH2M HILL will arrange for a contract laboratory program (CLP) type sample analysis of split environmental samples collected during the previous tasks.

Analytical Support and Data Validation (AN)
CH2M HILL will perform the validation of the split samples to ensure that adequate and definable sample management and techniques are implemented.

Data Evaluation (DE)
CH2M HILL will organize and evaluate data gathered during the previous tasks. The data evaluation activities will include:

- Data usability evaluation and field QA/QC
- Data reduction, tabulation, and evaluation

Step 2. Identify the Decision

(1) *Identify the principal study question* – The principal goal for CH2M HILL is to verify that the following study questions are adequately addressed by the Omega tenant and OPOG:

(a) What is the current nature and extent of contamination in surface and/or subsurface soil at the oil spill site near OW-1?

(b) Has all the oil-stained soil near OW-1 been removed?

(c) What is the current extent of 1,4-dioxane contamination in surface and/or subsurface soil at OU-1?

(d) Does the presence of 1,4-dioxane pose an unacceptable potential risk to human health and the environment?

(2) *Define alternate actions that could result from resolution of the principal study question* – These actions will be defined by the Omega tenant and OPOG, then reviewed by CH2M HILL.

(3) *Combine the principal study question and the alternative actions into a decision statement – The* decision statement for CH2M HILL is to verify that the Omega tenant and OPOG

generate sufficient data to resolve the four principal questions of the RI/FS and to take appropriate action based on the results of the investigation.

(a) The analytical results for soil samples will show the current nature and extent of contamination in surface and/or subsurface soil at the oil spill site near OW-1. Comparison of analytical results for the stained soil and for soil from the bottom and sides of the excavation will show whether the release also contained the chemicals of concern in addition to TPH expected for an oil spill.

(b) The analytical results for soil samples collected from the oil-spill excavation will show that the oil-stained soil near OW-1 been removed if TPH is not detected, or is at very low concentrations.

(c) The analytical results for soil samples will show the current extent of 1,4-dioxane contamination in surface and/or subsurface soil at OU-1.

(d) The analytical results for 1,4-dioxane will be evaluated for potential risk to human health and the environment.

(4) *Organize multiple decisions* – Based on the answer to the principal study question, decisions *about* additional phases of field investigative activities will be made by the Omega tenant and OPOG, then reviewed by CH2M HILL.

(a) If other contaminants of concern are detected in the stained soil, their concentrations will be compared to existing site investigation results to determine whether they were introduced into the soil by the oil spill or whether they were present at this location prior to the spill.

(b) If TPH is detected in the soil samples taken from the excavation, additional soil will have to be excavated and confirmation sampling repeated until all the oil-stained soil near OW-1 has been removed. TPH is expected to be the characteristic contaminant associated with the spill; other compounds may be identified under (a).

(c) Additional sampling may be recommended to characterize the current extent of 1,4-dioxane contamination in surface and/or subsurface soil at OU-1.

(d) Additional sampling may be recommended to assess the potential risk to human health and the environment from the presence of 1,4-dioxane at the site.

Step 3. Identify Inputs to the Decision

The purpose of this step is to identify the information and measurements needed to support the decision statement. The data will be used for comparison with data generated by the Omega tenant and OPOG. Further, the data will be evaluated with regard to the four principal questions of the oil-spill site and ongoing OU-1 RI/FS.

(1) Identify the information that will be required to resolve the decision statement –

(a) Soil analytical results from the removal action for the oil-spill site near OW-1: Analytical results for VOCs, SVOCs, metals, pesticides, and PCBs will be used to verify that the ongoing RI/FS has not been impacted by the oil spill.

(b) Analytical results for TPHg and TPHd will be used to verify that the spill-contaminated soil has been removed.

(c) Soil 1,4-dioxane results from the OPOG ongoing RI/FS at OU-1.

(d) Soil 1,4-dioxane results from the OPOG ongoing RI/FS at OU-1.

(2) *Determine the sources for each item of information identified:* Soil analytical results.

(3) *Identify the information that is needed to establish the action level* –

(a) Action level guidance for TPH (gasoline and diesel) will be based on the Leaking Underground Fuel Tank (LUFT) Field Manual, Guidelines for Site Assessment, Cleanup, and Underground Storage Tank Closure (October, 1989). Action level guidance for VOCs, SVOCs, pesticides and PCBs, and metals will be based on EPA Preliminary Remediation Goals (PRGs) for residential and/or industrial soils.

(b) Action level guidance for TPH (gasoline and diesel) will be based on the LUFT Field Manual, Guidelines for Site Assessment, Cleanup, and Underground Storage Tank Closure (October, 1989).

(c) Action level guidance will be based upon EPA Preliminary Remediation Goals (PRGs) for residential and/or industrial soils.

(d) Action level guidance will be based upon EPA Preliminary Remediation Goals (PRGs) for residential and/or industrial soils.

(4) *Confirm that appropriate measurement methods exist to provide the necessary data* – The methods that have been identified to meet project needs are provided in the main text of this QAPP Addendum 01 (April 2004).

Step 4. Define the Boundaries for the Study

The oil spill site is within close proximity to groundwater monitoring well OW-1, at the former Omega Chemical recycling facility. Soil sampling and excavation activities will be limited to the boundaries of this property.

The OU-1 area was defined in the Consent Decree as extending from the former Omega Chemical property to 100 feet southwest of Putnam Street. The sample locations and analytical methods were defined in the EPA-approved Sampling and Analysis Plan for OPOG (CDM, 2003). Soil sampling for 1,4-dioxane will be limited to the OU-1 area.

(1) *Specify the characteristics that define the population of interest* – The samples will be *collected* following a systematic, rather than statistical, sampling design.

(a) Concentrations of contaminants of concern in surface and/or subsurface soil at the oil spill site near OW-1.

(b) TPH concentrations in soil near OW-1.

(c) Concentrations of 1,4-dioxane contamination in surface and/or subsurface soil at OU-1.

(d) Concentrations of 1,4-dioxane contamination in surface and/or subsurface soil at OU-1.

(2) *Define the spatial boundary of the decision statement* –

(a) Define the geographical area to which the decision statement applies –

Oil spill site sampling locations will be limited to the area of excavation; they will be selected by the Omega tenant. The 1,4-dioxane sampling locations were selected by OPOG; they are shown in Figure 4-1 of the original FSP (EPA, 2004b).

(3) *Define the temporal boundary of the decision statement* –

(a) Determine the timeframe to which the decision statement applies –

The oil spill investigation is anticipated to take place in April 2004. The duration of the investigation is at the discretion of the Omega tenant.

The OU-1 RI/FS investigation is currently ongoing and will continue at the discretion of OPOG.

(b) Determine when to collect data – Data will be collected during the timeframe specified in (a).

(4) *Define the scale of decisionmaking – The scale of decisionmaking will be limited to the OU-1 area.*

(5) *Identify practical constraints on data collection – The sampling locations and schedule will depend on field activities conducted by the Omega tenant and OPOG.*

Step 5. Develop a Decision Rule

(1) *Specify the statistical parameter that characterizes the population of interest* -

(a) Split sample analysis results at the oil spill site will be compared to the Omega tenant's analysis results.

(b) Split sample analysis results at the oil spill site will be compared to the Omega tenant's analysis results.

(c) The 1,4-dioxane analysis results will be compared with OPOG's data. A factor-difference will be determined for each sampled media and compound.

(d) Sample analysis reports will be compared to action levels. Each value, not a statistical parameter such as mean concentration, will be evaluated against the action levels.

(2) *Specify the action level for the study* – Factor-difference action levels will be used.

(3) *Develop a decision rule (an "if...then..." statement)* – If the factor-difference between the split sample and the Omega tenant's/OPOG's analytical results is greater than an action limit to be established, resampling by the Omega tenant/OPOG may be requested as a result. The action limit will be established based on professional judgement.

Step 6. Specify Tolerable Limits on Decision Errors

Tolerable limits on decision errors, which are used to establish performance goals for the data collection design, are specified in this step.

(1) *Determine the range of the parameters of interest* – There are no historical data on TPH at the site. The available historical range of the remaining parameters of interest is presented in the original QAPP (EPA, 2004a). Regulatory action levels for the parameters of interest are summarized in Tables A-1a and A-1b of this QAPP Addendum 01. These values constitute the range of interest for the parameters of interest.

(2) *Identify the decision errors and choose a null hypothesis* – The DQO guidance prescribes the identification of the null hypothesis and associated decision errors for *determining* the number of random samples and the locations to attain a given level of confidence with the spatial distribution. Because samples will be collected at systematically selected locations, statistical decision errors cannot be defined. However, project error tolerances are defined in terms of precision, accuracy, representativeness, comparability, and completeness (PARCC) parameters in this QAPP Addendum. Analyte-specific accuracy and precision ranges are shown in Table A-2 of this QAPP Addendum 01. The project completeness goal is set at 90 percent.

Step 7. Optimize the Design

The Wok Plan was optimized to focus on collection of split and duplicate samples and their analysis.

(1) *Review the data quality objective (DQO) outputs and existing data* –

(a) The data will be compared to existing site data and regulatory action levels.

(b) The data will be compared to existing site data and regulatory action levels.

(c) The data will be compared to existing site data and regulatory action levels.

(d) Existing (i.e., historical) data will be included in the risk assessment.

(2) *Develop general data collection design alternatives* – None anticipated.

(3) *For each data collection design alternative, select the optimal sample size that satisfies the objectives* - None anticipated.

(4) *Select the most resource-effective data collection design that satisfies the DQOs* – The number of split/duplicate samples will be 10 percent (20 percent for soil samples) of the field *samples* collected by OPOG. When 10 percent of OPOG's samples is less than one, one sample will be collected. The number of samples for the oil-spill was determined based on the anticipated extent of the contamination.

(5) *Document the operational details and theoretical assumptions of the selected design in the sampling and analysis plan* –

(a) One split sample will be collected from the excavated soil near the OW-1 oil spill site to characterize the nature of contamination; two split soil samples will be collected below the excavation site to verify all contaminated soil has been removed. Split sampling results will be compared to the tenant's results.

(b) One split sample will be collected from the excavated soil near the OW-1 oil spill site to characterize the nature of contamination; two split soil samples will be collected below the excavation site to verify all contaminated soil has been removed; and one split sample will be collected from the backfill material to verify that clean soil was used. Split sampling results will be compared to the tenant's results.

(c) Split soil samples will be collected at locations, determined by OPOG, for 1,4-dioxane characterization at OU-1. This investigation is part of the ongoing OPOG RI/FS investigation at OU-1. The split sampling results will be compared to OPOG's results.

(d) All existing (i.e., historical) data will be included in the risk assessment.

Appendix B
Analytical Technical Specifications

Appendix B
Analytical Technical Specifications

Contents

Appendix B-1
Total Petroleum Hydrocarbons

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE #385

EXTRACTABLE PETROLEUM HYDROCARBONS BY GC/FID

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Signature	Title	Date
_____	_____	_____
_____	_____	_____
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STANDARD OPERATING PROCEDURE #385

EXTRACTABLE PETROLEUM HYDROCARBONS BY GC/FID

This SOP was prepared by Lockheed Martin for the United States Environmental Protection Agency (USEPA) under the Environmental Services Assistance Team (ESAT) contract (EPA contract No. 68D60005).

APPROVED BY:

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ESAT Document Control Number: ESAT-9B-1853

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1 SCOPE AND APPLICATION

1.1 This method describes the procedures used to analyze methylene chloride extracts for hydrocarbons in the C_{10} to C_{40} range; this range includes oils as well as fuels. Gas chromatography with flame ionization detection is used for the quantitative and qualitative determination of hydrocarbons. The identification of specific fuel types, if necessary, may be complicated by environmental processes such as evaporation, biodegradation, or the presence of more than one fuel type.

1.2 This method is applicable to the determination of kerosene, diesel, motor oil or other hydrocarbons in the carbon number range of 10 to 40 in extracts prepared from solid or liquid samples. Estimated quantitation limits are 250 g/L in aqueous samples and 5 mg/kg in soil samples for kerosene and diesel range hydrocarbons and 1,000 g/L and 20 mg/kg, respectively, for oil range hydrocarbons. This SOP is based on procedures contained in EPA SW-846 method 8015B.

2 METHOD SUMMARY

Sample extracts, which have been fortified with surrogate analytes, are injected into a gas chromatograph with a flame ionization detector (FID). Sample components are separated in the fused-silica capillary gas chromatographic column during temperature programming, then detected by the FID.

The fuel of interest is quantitated by comparing its area sum response over the retention time range which it elutes to the area sum response of a fuel standard analyzed under the same conditions as the sample. Probable identification of fuels in samples, if needed, is done by comparing the chromatographic pattern generated by analysis of the sample to the chromatographic pattern of fuels analyzed under the same conditions as the sample.

3 DEFINITIONS

3.1 Quantitation Limit (QL) - The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The QL is the concentration of the lowest non-zero standard in the calibration curve. Sample QL's are highly matrix-dependent.

3.2 FID - Flame ionization detector.

3.3 Laboratory Fortified Blank (LFB) - An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed

exactly like a sample, and its purpose is to determine if the methodology is in control, and if the laboratory is capable of making accurate and precise measurements.

3.4 Laboratory Fortified Sample Matrix (LFM) and Laboratory Fortified Sample Matrix Duplicate (LFMD) - Two aliquots of the same environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM and LFMD are analyzed exactly like a sample, and their purpose is to determine whether the sample matrix contributes bias to the analytical results and to indicate the precision associated with laboratory procedures. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM and LFMD corrected for background concentrations.

3.5 Laboratory Reagent Blank (LRB) - An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 Method Detection Limit (MDL) - The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix type containing the analyte.

3.7 Quality Control Sample (QCS) - A solution of method analytes of known concentrations which are used to prepare mid level standard(s). The QCS solution is obtained from a source different from the source of calibration standards. It is used to check the accuracy of the initial calibration solutions.

3.8 Stock Standard Solution (SSS) - A concentrated solution containing one or more method analytes purchased from a reputable commercial source.

3.9 Surrogate Analyte (SA) - A pure analyte which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in a known amount before extraction or other processing, and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

3.10 Quantitation Limit Standard (QLS) - The lowest level CAL solution. The QLS is used to verify analytical system response at the quantitation limit.

3.11 TPH - Total Petroleum Hydrocarbons.

4 HEALTH & SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals should be minimized. When using any solvent certain safety precautions must be taken. Protective clothing (lab coats) and safety glasses must always be worn when handling solvents. Solvent transfer and handling should be conducted under a hood whenever possible, to prevent inhalation of vapors. Contact lenses must not be worn by extraction personnel. In case of exposure, notify a supervisor or the Health and Safety Coordinator to determine if additional medical attention is needed. Material safety data sheets (MSDS) are available to all personnel involved in the chemical analysis in the library (Room 118) or Room 413.

4.2 Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Stock standard solutions of these compounds must be prepared in a hood. Routine procedures in this SOP do not require contact with concentrated solutions or neat materials. All standard preparation procedures associated with this SOP should be performed in a hood.

4.3 Methylene chloride is a suspected carcinogen. Effects of overexposure: acute inhalation or ingestion causes mild central nervous system depression. The primary toxic effect is narcosis. Other toxic effects are pulmonary edema, encephalopathy, and hemolysis. Methylene chloride irritates the eyes, skin, and respiratory tract. No systemic effects have been reported in humans, although excessive concentrations have caused cancer and liver and kidney damage in animals. Emergency and first aid - Inhalation: immediately remove to fresh air. If not breathing, administer mouth-to-mouth rescue breathing. If there is no pulse, administer cardiopulmonary resuscitation (cpr). Contact physician immediately. Eye contact: flush with water continuously for 15 minutes. Get emergency medical assistance. Skin contact: flush thoroughly for at least 15 minutes. Wash affected skin with soap and water. Remove contaminated clothes and shoes. Get emergency medical assistance. Ingestion: call local poison control center for assistance. Contact physician immediately. Never induce vomiting or give anything by mouth to a victim unconscious or having convulsions.

4.4 Acetone liquid and vapors are highly flammable. Avoid heat, sparks, open flame, open containers, and poor ventilation. Effects of overexposure: Acetone is a mild eye and mucous membrane irritant, primary skin irritant, and central nervous system depressant. Acute exposure irritates the eyes and upper respiratory tract. Direct skin contact produces dermatitus, characterized by dryness and erythema through defatting of skin. High concentrations produce narcosis and hypoglycemia. Emergency first aid - Inhalation: immediately remove to fresh air. If not breathing, administer mouth-to-mouth rescue breathing.

If there is no pulse, administer cardiopulmonary resuscitation (cpr). Contact physician immediately. Eye contact: flush with water continuously for 15 minutes. Get emergency medical assistance. Skin contact: flush thoroughly for at least 15 minutes. Wash affected skin with soap and water. Remove contaminated clothes and shoes. Wash clothing before re-use, and discard contaminated shoes. Get emergency medical assistance. Ingestion: call local poison control center for assistance. Contact physician immediately. Never induce vomiting or give anything by mouth to a victim unconscious or having convulsions.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Sample extracts for GC analysis are received from the extraction lab personnel and custody transferred to the GC laboratory staff by signing the appropriate sections in the extraction logbook. Copies of tracking sheets, chain-of-custody records, extraction logbook pages, and moisture determination records should accompany the sample extracts.

5.2 The extracts are marked with the Region 9 Laboratory number, which can be checked against the tracking sheets and chain-of-custody record to determine the Client sample number, Case number, and Sample Delivery Group number.

5.3 Sample extracts may be stored in the refrigerator maintained at 4°C ± 2°C in Room 400 prior to analysis. Sample extracts must be analyzed within 30 days of extraction. Maintain a refrigerator temperature log daily. Report deviations following SOP # 805.

5.4 Following analysis and submission of the data deliverables for a SDG the extracts must be stored under refrigeration an additional 90 days before segregating for disposal. The sample results and preparation information are used to determine proper disposal.

6 INTERFERENCES

6.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus that lead to anomalous peaks or elevated baselines in chromatograms.

6.2 Phthalate esters are commonly used as plasticizers and are easily extracted from plastic materials. Contact of samples, solvents, reagents, glassware, extracts, or other sample processing apparatus with plastics must be avoided.

6.3 Interfering contamination may occur when a sample containing low concentrations of compounds is analyzed immediately after a sample containing relatively high concentrations of compounds. Syringes and splitless injection port liners must be cleaned carefully or replaced as

needed. After analysis of a sample containing high concentrations of compounds, a laboratory instrument blank should be analyzed to ensure that accurate values are obtained for the next sample.

6.4 Interfering contamination may occur when a sample containing oil range hydrocarbons, especially with carbon numbers exceeding C_{40}, is analyzed. After analysis of a sample containing oil range hydrocarbons, a laboratory instrument blank should be analyzed to ensure that accurate values are obtained for the next sample. The column may need to be heated to an elevated temperature, not exceeding the column limit, until the baseline returns to previous levels. Syringes and splitless injection port liners must be cleaned carefully or replaced as needed.

7 APPARATUS AND MATERIALS

7.1 Instrumentation

7.1.1 Gas chromatograph with FID detector and splitless injection port (Hewlett Packard 5890, or equivalent).

7.1.2 Fused Silica Capillary Gas Chromatography Column -- Any capillary column with a phase ratio (β) of about 265 that provides adequate resolution and capacity may be used. The column used for method validation was 30 m x 0.53 mm x 0.5 μm Rtx - 1.

7.1.3 Data Acquisition and Processing System -- Able to control the GC and to acquire, store, and process gas chromatographic data. The software must be able to calculate response factors and the concentrations of analytes in samples. HP EnviroQuant ChemStation software and data acquisition computers (or equivalent).

7.2 Reagents and Standards

7.2.1 Acetone - capillary GC/GC-MS solvent grade

Caution: Acetone liquid and vapors are highly flammable. See Health and Safety summary for precautions (Section 4.4).

7.2.2 Methylene chloride - recycled and capillary GC/GC-MS solvent grade

Caution: Methylene chloride is a suspected carcinogen. See Health and Safety summary for precautions (Section 4.3).

7.2.3 Surrogate Spiking Solution - Solution of n-hexacosane (n-$C_{26}H_{54}$) in methylene chloride:acetone 2:1v/v at 2,500 µg/mL. Prepare from neat n-hexacosane by weighing 125 mg n-hexacosane into a 50 mL volumetric flask, dissolving it in 33 mL of methylene chloride (may require sonication or warming) and diluting to volume with acetone. Document standard preparation in the Semivolatile Standards Logbook following EPA Region 9 Laboratory SOP # 840, Notebook Documentation and Control.

7.2.4 Instrument Blank - Solution of n-hexacosane in methylene chloride at 50 µg/mL. Prepare from the surrogate spiking solution by diluting 1 mL to 50 mL in methylene chloride. Document standard preparation in the Semivolatile Standards Logbook following EPA Region 9 Laboratory SOP # 840, Notebook Documentation and Control.

7.2.5 Stock Standard Solutions - Individual solutions of analytes purchased from commercial suppliers, such as Restek #31258 (XHc Diesel Fuel #2 Composite Standard), or equivalent, or Restek #31256 (XHc Kerosene Composite standard), or equivalent, or Restek #31464 (Motor Oil Composite Standard), or equivalent, or a homologous n-alkane series covering the carbon number range of interest. These solutions are diluted with methylene chloride to make the calibration solutions. Store in amber vials under refrigeration.

Note: Whenever possible, the instrument should be calibrated using a sample of the fuel or oil that is contaminating the site. The calibration standard should be selected prior to the start of the project in conjunction with the client. A different calibration standard may be required if the fuel type in the sample does not match the calibration standard.

7.2.6 TPH Matrix Spiking Solution - A solution of the fuel of interest at a concentration of 2,500 µg/mL in acetone. This solution is valid for six months from the date of preparation, or until ongoing QC indicates a problem. Document standard preparation in the Semivolatile Standards Logbook following EPA Region 9 Laboratory SOP # 840, Notebook Documentation and Control.

7.2.7 Calibration Solutions - Prepare calibration solutions for the fuel of interest at five concentrations in methylene chloride using the stock standard and surrogate spiking solutions. These solutions are valid for six months from the date of preparation, or until ongoing QC indicates a problem. A standard can also be prepared from a homologous n-alkane series covering the expected carbon number range. Oil range standards need to be at higher concentrations. Document standard preparation in the Semivolatile Standards Logbook following EPA Region 9 Laboratory SOP # 840, Notebook Documentation and Control.

7.2.7.1 This table is applicable for stock standard solutions at 50,000 µg/mL and surrogate spike solutions at 2,500 µg/mL.

SOLUTION	VOLUME USED	FINAL VOLUME	FINAL CONCENTRATION
Stock Standard Surrogate Spike	10 µL 40 µL	10 mL 10 mL	50 µg/mL 10 µg/mL
Stock Standard Surrogate Spike	30 µL 100 µL	10 mL 10 mL	150 µg/mL 25 µg/mL
Stock Standard Surrogate Spike	100 µL 200 µL	10 mL 10 mL	500 µg/mL 50 µg/mL
Stock Standard Surrogate Spike	250 µL 300 µL	10 mL 10 mL	1250 µg/mL 75 µg/mL
Stock Standard Surrogate Spike	800 µL 400 µL	10 mL 10 mL	4000 µg/mL 100 µg/mL

7.2.7.2 Prepare calibration solutions from neat fuels or oils by first determining the density of the hydrocarbon fuel mixture by taring a 10 mL volumetric flask, then filling it to the mark with the neat fuel, at room temperature, and weighing it to the nearest 0.0001 gram. Divide the net weight by 10 to obtain the density in grams/mL. Use the experimentally determined density in the following calculations.

Prepare a 4000 mg/L (nominal) range standard by injecting 5 L of neat standard per mL of dichloromethane. The actual concentration, in mg/L, will be 5000 times the density of the neat fuel in g/mL. For example, injecting 250 L of Kerosene into about 49 mL of solvent in a 50 mL volumetric flask, then adding additional solvent to volume, would result in a 3,910 mg/L standard assuming a density of 0.782 g/mL for Kerosene.

If the neat standard, such as motor oil, is too viscous to measure with a microliter syringe, weigh out about 200 mg (0.2 g) using an analytical balance and dilute to 50 mL with dichloromethane.

Prepare the other calibration solutions by serially diluting the 4,000 mg/L standard. Document standard preparation in the Semivolatile Standards Logbook following EPA Region 9 Laboratory SOP # 840, Notebook Documentation and Control.

7.2.8 Calibration Verification Solution - Equivalent to the mid-point initial calibration solution but prepared separately.

7.2.9 Quantitation Limit Standard (QLS) - Equivalent to the lowest level calibration standard. The QLS is used to verify instrument response at the quantitation limit.

7.2.10 Quality Control Sample (QCS) - Equivalent to the mid-point initial calibration solution but prepared from a source different from the source of calibration standards. The QCS is used to check the accuracy of the initial calibration solutions.

7.3 Glassware and Incidentals

7.3.1 Volumetric flasks, type A, 100-mL, 50-mL, 25-mL, and 10-mL.

7.3.2 Microliter syringes (10-μL, 25-μL, 50-μL, 100-μL, 250-μL, 500-μL, and 1-mL).

8 QUALITY CONTROL

8.1 Quality control requirements include instrument calibration, calibration verification, quantitation limit verification, determination of retention time windows, and the initial demonstration of laboratory capability followed by regular analyses and monitoring of laboratory reagent blanks, laboratory fortified blanks, and laboratory fortified matrix samples.

8.2 The GC system must be calibrated whenever corrective action which may change instrument response (e.g., detector gas adjustment, column replacement, etc.) is performed or if the calibration verification criteria can not be met.

8.2.1 Analyze the initial calibration standards according to Section 9 of this SOP.

8.2.2 Obtain area sums for each fuel mixture or homologous n-alkane series over the retention time range during which at least 90% of the material elutes. The approximate carbon number ranges are C_{10} to C_{16} for kerosene and C_{12} to C_{26} for Diesel. All sample components eluting after C_{26} are considered oil range.

Draw a manual baseline if the baseline drawn by the data system integrator does not accurately reflect the total area response, including the unresolved area that lies below the individual peaks, of the fuel in the sample. Draw a manual baseline from the point where the baseline starts to deviate from the trend to a second inflection point in the chromatogram, or to the end of the chromatogram if there is no second inflection point. See Appendix B for examples.

8.2.3 Manual integrations must conform to EPA Region 9 SOP 835, *Chromatographic Integration Procedures.*

8.2.3.1 Print a view of the chromatogram to be reintegrated using QEDIT. Indicate the reasons for manually integrating the chromatographic results on the chromatogram and initial and date the statement.

8.2.3.2 Reintegrate the chromatogram and print the new view. Save the reintegrated value(s). Document the manual integration on the reintegrated chromatogram and initial and date the statement.

8.2.3.3 After all manual integrations have been completed, print the new quant report. Ensure that each manual integration is indicated on the new quant report. Indicate the fact that there was manual integration in the instrument run log.

8.2.3.4 Show the chromatograms, quant reports and log book to a supervisor, QA/QC coordinator or team leader for review and acceptance.

8.2.4 The data system calculates the response factor (RF) for the target fuel or n-alkane mixture from its area sum response and for the surrogate for all five calibration standards using Equation 1.

Eq. 1

$$RF = (A_x)/ (C_x)$$

Where

Ax = Area of compound x

Cx = Mass of compound x injected (ng)

8.2.5 Calculate the average RF for all analytes.

8.2.6 Calculate the percent relative standard deviation (%RSD) of the RF values for each compound using Equation 2.

EQ. 2

$$\%RSD = (SD/ RF_{avg}) \times 100$$

$$SD \sqrt{\frac{\sum_{i\ 1}^{n} (x_i\ x_{ave})^2}{n\ 1}}$$

8.2.7 Verify that both the target fuel and the surrogate pass the requirement of %RSD less than or equal to 20% immediately after the initial calibration is finished.

If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the failed one in the ICAL. If more than one standard fails, corrective action is required.

8.2.8 Analyze a QCS sample immediately after each initial calibration. The RF for the QCS must be within 30% of the mean RF in the initial calibration. If the QCS sample fails, the cause must be determined and corrected before analysis of samples can proceed.

Note: Fuel standards from different sources may contain different compound mixes and therefore may not be reliable for verifying calibration standards.

8.2.9 If the initial calibration meets the criteria, the remainder of the 12-hour analytical period may be used for the analysis of blanks and samples, using the average response factors from the initial calibration to quantitate field and QC sample data.

8.3 Analyze a calibration verification standard at the beginning of each 12-hour analytical period and at the end of the 12-hour analytical period. The 12-hour analytical period begins with the injection of the calibration verification standard and ends with the completion of analysis of the last sample that can be injected within 12 hours of the beginning of the period. Analysis of calibration verification standards, bracketed by instrument blanks, after every ten samples is recommended. The calibration verification standard is used to validate the initial calibration for the samples run during the associated 12-hour time period.

8.3.1 Analyze the calibration verification standard according to Section 9 of this SOP.

8.3.2 Calculate the response factor (RF) for the target fuel from its area sum response and for the surrogate compound using Equation 1.

8.3.3 Calculate the percent difference (%D) between the calibration verification RF and the initial calibration average RF for the target fuel and the surrogate using Equation 3.

EQ 3.

$$\%D \quad \frac{RF_c \quad RF_{avg}}{RF_{avg}} \times 100$$

8.3.4 The percent difference must be less than or equal to 15% for both analytes. If either of the analytes fail this criteria a second calibration verification may be analyzed. Repeated failure requires that the cause be determined and corrected. If repairs to the system are required then a new initial calibration must be performed. The analyst should observe trends in the data such as declining response, erratic response, etc. which may signal the need for instrument maintenance.

8.3.5 Acceptable sample analyses must be bracketed by the analyses of calibration verification standards that meet QC limits. If a calibration verification sample fails, a second calibration verification sample may be analyzed. Repeated failure requires that corrective action be taken to restore the system before any additional samples are analyzed. All affected samples must be re-analyzed.

8.4 Analyze a quantitation limit standard (QLS) in each 12-hour period when analyses of field or QC samples are performed. The QLS is used to verify analytical system response at the quantitation limit.

8.4.1 Analyze a standard of the fuel of interest at the concentration of the lowest initial calibration level according to Section 9 of this SOP.

8.4.2 Calculate the concentration of the target fuel.

8.4.3 Calculate the percent of true value for the target fuel using Equation 4.

EQ. 4

$$\% \text{ True Value} = (Cd / Tv) \times 100$$

Where:

Cd = Concentration determined by analysis
Tv = True value

8.4.4 The accuracy for each analyte, expressed as a percentage of true value must be between 50 - 150%. If the QLS sample fails, a second QLS sample may be analyzed. Repeated failure requires that the cause be determined and corrected before analysis of samples can begin. If repairs to the system are required then a new initial calibration must be performed.

8.5 Analyze an instrument blank after the initial calibration or calibration verification is performed and before samples are analyzed. The instrument blank chromatogram and quantitation report must be checked to insure it contains less than or equal to one-half the QL of the target compounds. It is also important to monitor the chromatographic baseline to insure there are no humps or disruptions which could be integrated as peak area when sample constituents elute on top of them. If the instrument blank meets these requirements sample analysis may proceed.

8.6 Surrogate Recovery

8.6.1 Calculate the surrogate recovery in all field and QC samples immediately after analysis using the following formula:

EQ. 5

$$\%R = (\text{Amount Found}/\text{Amount Spiked}) \times 100.$$

8.6.2 The surrogate recovery must be between 70% and 130%.

8.6.3 Take the following steps if surrogate recovery is not within the limits.

8.6.3.1 Check to ensure that there are no calculation errors, and check the system performance.

8.6.3.2 Re-analyze the extract if a system performance problem or calculation error is not evident. The extract may be diluted for re-analysis if examination of the chromatogram so indicates.

8.6.3.3 If re-analysis of the extract does not solve the problem, the sample may have to be re-extracted. Corrective action is decided by the EPA WAM on a case by case basis.

8.6.3.4 Do not re-extract undiluted samples with surrogate recoveries outside the limits if the diluted analysis with acceptable surrogate recoveries is being submitted. Report the event in the runlog and report narrative.

8.6.3.5 Do not re-analyze the LFM or LFMD samples, even if the surrogates recoveries are outside the limits.

8.6.3.6 If the sample associated with the LFM/LFMD analyses does not meet the surrogate recovery criteria, it should be reanalyzed only if the matrix spike and duplicate surrogates recoveries are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need re-analysis. The similarity in surrogates recoveries in the sample and spike analyses must be discussed in the report narrative

8.6.4 If the surrogate recoveries of the re-analysis of the extract are within limits, then:

8.6.4.1 If the re-analysis was undiluted, the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses. Distinguish between the analysis and re-analysis by adding an "RI" suffix to the client sample ID on the re-analysis. The problem must be documented in the report narrative.

8.6.4.2 If the re-analysis was diluted, the problem was a matrix effect. Report the results from the re-analysis and submit the data from both analyses and discuss the result in the report narrative. Distinguish between the undiluted and diluted analysis by adding a "DL" suffix to the client sample ID on the diluted analysis. The problem must be documented in the report narrative.

8.6.5 If the surrogate recoveries of the re-extraction are within limits, then the problem was within the laboratory's control. Report the results from the re-extraction. Distinguish between the original analysis and the re-analysis by adding the "RE" suffix to the client sample ID in the re-analysis. The problem must be documented in the report narrative.

8.6.6 If the re-extraction does not solve the problem, report the results from the first analysis and submit the data from both analyses. Distinguish between the original analysis and the re-analysis by adding the "RE" suffix to the client sample ID in the re-analysis. The problem must be documented in the report narrative.

8.7 Calculate absolute retention time windows for each analyte and surrogate on each chromatographic column and instrument. New retention time windows must be established when a new GC column is installed. Before establishing retention time windows, make sure that the chromatographic system is operating reliably and that the system conditions have been optimized for the target analytes and surrogates in the sample matrix to be analyzed.

8.7.1 Make three injections of a homologous n-alkane series covering the carbon number range of interest over the course of a 72-hour period. Serial injections or injections over a period of less than 72 hours may result in retention time windows that are too tight.

8.7.2 Record the retention time for the defining n-alkanes (e.g. C_{12} and C_{26} for Diesel) and the surrogate to three decimal places (e.g., 9.007). Calculate the mean and standard deviation of the three absolute retention times for each defining n-alkane and the surrogate.

8.7.3 If the standard deviation of the retention times for a target compound is less than 0.01minutes then use a default standard deviation of 0.01 minutes.

8.7.4 The width of the retention time window for the surrogate is defined as ±3 times the standard deviation of the mean absolute retention time established during the 72-hour period. If the default standard deviation in Section 8.7.3 is employed, the width of the window will be 0.03 minutes.

8.7.5 The retention time range for a fuel is the lower limit of the retention time window for the n-alkane at the start of the carbon number range and the upper limit of the retention time window for the n-alkane at the end of the carbon number range for the fuel (e.g. C_{12} and C_{26} for Diesel).

8.7.6 Establish the center of the retention time window for each fuel and the surrogate by using the average retention time(s) from the initial calibration.

8.7.7 All surrogates or n-alkanes in the calibration verification standard must fall within the established retention time windows. If the retention time does not fall within the retention time window, then take corrective action to restore the system. If repairs to the system are required then a new initial calibration must be performed.

8.8 The laboratory must perform an initial demonstration of capability with each sample preparation technique used in analyzing analytes of interest with this SOP before analyzing any samples. See EPA Region 9 SOP #880, *Initial and Continuing Demonstration of Capabilities and Performance* for requirements and procedures.

8.8.1 Analyze laboratory fortified blanks containing Diesel at a suggested concentration of 2,500 µg/L for water or 50 mg/Kg for soil to demonstrate precision and accuracy.

8.8.2 Analyze laboratory fortified blanks containing Diesel at approximately 250 µg/L for water or 5 mg/Kg for soil to determine the MDL.

8.9 Extract an LRB with each extraction batch to demonstrate that the entire analytical system - from extraction through GC analysis - is free of contamination.

8.9.1 Analyze the LRB according to Section 9 of this SOP.

8.9.2 Evaluate the LRB as soon as possible after it has been analyzed to determine if the following criteria have been met:

The LRB is acceptable if it contains less than the quantitation limit (QL) of any fuel of interest.

8.9.3 The LRB surrogate recoveries must meet the criteria listed in Section 8.6.

8.9.4 Corrective action - If the LRB is not acceptable, the source of the contamination must be found and eliminated and the problem documented before analysis can proceed. If re-analysis does not solve the problem, the batch may have to be re-extracted. Corrective action is decided by the EPA WAM on a case by case basis

8.9.5 If the surrogate recovery does not meet acceptance criteria, re-analyze the extract. If the surrogate recovery still does not meet acceptance criteria, the batch may have to be re-extracted. Corrective action is decided by the EPA WAM on a case by case basis.

8.10 Laboratory Fortified Blank (LFB) An LFB is analyzed to demonstrate that the analytical system is in control. The LFB is extracted and analyzed once per extraction batch or every 20 samples, whichever is more frequent. The LFB is an LRB spiked with laboratory fortified matrix solution.

8.10.1 Analyze an LFB containing the target fuel at a concentration of 2,500 µg/L for water or 50 mg/Kg for soil according to Section 9 of this SOP.

8.10.2 Calculate the percent of true value using Equation 4 in Section 8.4.3.

8.10.3 The accuracy, expressed as a percentage of true value, must be between 70% and 130%. If acceptable accuracy cannot be achieved, the problem must be located and corrected prior to reporting any sample data and before additional samples are analyzed.

8.11 Laboratory fortified matrix and duplicate analysis.

8.11.1 A laboratory fortified matrix and duplicate sample is extracted and analyzed for each batch of twenty or fewer samples extracted as a group. Matrix QC samples are usually designated in the field. In the event that a sample was not designated as the laboratory fortified matrix spike sample and adequate sample volume exists, the analyst will choose one representative sample from the SDG for QC analysis. The analyst shall not designate any obvious field blanks as the QC sample.

8.11.2 Analyze LFM and LFMD extracts as soon as possible following the analysis of the sample designated as the laboratory fortified matrix sample.

8.11.3 Analyze the LFM and LFMD according to Section 9 of this SOP.

8.11.4 Calculate the recovery of each compound using Equation 6.

EQ 6

$$\% \text{ Rec} = ((SSR - SR)/SA) \times 100$$

where,

SSR = Spiked sample result
SR = Sample result
SA = Spike added

8.11.5 Calculate the relative percent differences (RPD) of the recoveries of each compound in the LFM and LFMD using Equation 7.

EQ. 7

$$RPD = \frac{(LFMC - LFMDC)}{(LFMC + LFMDC)/2} \times 100$$

where:

LFMC = Measured concentration of analyte in LFM
LFMDC = Measured concentration of analyte in LFMD

8.11.6 Acceptance criteria: The percent recovery (%R) must be between 65% and 135% and the relative percent differences (RPD's) must be ≤25%.

The limits for LFM/LFMD recovery are advisory limits only. If the limits are not met, then no further action is required, as long as the LFB is within limits, since the purpose of these analyses is to determine matrix effects on compound recovery. However, frequent failure to meet the recovery or RPD criteria should alert the analyst that a problem may exist and must be investigated. The analyst should analyze the matrix spike solution and check the recoveries of the spike compounds. A new solution should be prepared if the recoveries are not within 20% of expected.

8.12 The table below lists the action to be taken based on the LFB and LFM/LFMD results.

QC ACCEPTANCE MATRIX

+ = PASS = FAIL

CASE	1	2	3	4	5	6	7	8
LFB - % REC	+	+	+	+				
LFM/LFMD -% REC	+		+		+		+	
LFM/LFMD - RPD	+	+			+	+		

Case 1: Extraction batch acceptable.

Case 2: Extraction batch acceptable; matrix effect confirmed.

Cases 3 & 4: Extraction batch is unsatisfactory. Investigate LFM/LFMD problem and document findings in report narrative.

Case 5: Extraction batch rejected. Batch may have to be re-extracted unless LFB problem is determined and documented.

Cases 6, 7 & 8: Extraction batch rejected. Re-extract batch.

8.13 Sample dilution.

8.13.1 Dilute and inject a new aliquot of the extract if the on-column concentration of the fuel of interest in any sample exceeds the initial calibration range. Use the following criteria in performing dilutions:

8.13.1.1 Use the results of the original analysis to determine the approximate dilution factor required to get the fuel of interest within the initial calibration range.

8.13.1.2 Keep the response of the fuel of interest in the upper half of the initial calibration range of the instrument by choosing an appropriate dilution factor.

8.13.1.3 Do not dilute LFM/LFMD samples to get either the spiked or non-spiked target compounds within the initial calibration range. If the sample from which the spike aliquots were taken contains high levels of the spiked analytes, calculate the concentration and recovery of the analytes from the undiluted analysis, and note the problem in the report narrative.

8.13.1.4 In the case of extremely contaminated samples several dilutions may be required.

8.13.1.5 Distinguish between the undiluted and diluted analysis by adding a "DL" suffix to the client sample ID on the diluted analysis.

8.13.2 Demonstrate that there is no carryover to subsequent analyses after a sample is analyzed that contains compounds at a level exceeding the initial calibration range of the system. This can be done by analyzing an instrument blank.
Monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample that exceeded the limits above. The maximum contamination criteria are as follows:

The sample should not contain a concentration above the QL for the target compound that exceeded the limits in the contaminated sample.

8.13.3 The most common cause of carryover is hydrocarbon in the oil/asphalt range. This may require cleaning the injection port and analyzing an instrument blank.

9 ANALYTICAL PROCEDURES

9.1 Demonstration and documentation of acceptable initial calibration are required before any samples are analyzed and is required intermittently throughout sample analysis as dictated by results of calibration verification checks. After initial calibration has been successfully accomplished, a calibration verification and quantitation limit check are required each 12-hour work shift in which analyses are performed.

9.2 Recommended GC operating parameters (method TPHD.M):

Injector temperature - 310°C
Detector temperature - 330°C
Injection conditions - 2 uL, splitless — Purge B off at injection
Purge B on at 0.50 min
Column flow - Rtx-1 - head pressure 4.8 psig
- flow at 50°C: 8.3 mL/min
Temperature program - 50°C, hold 2 min.
- 12°C/min to 310°C, hold 20.33 min.
Detector gases - He make-up - 22.8 mL/min
- H_2 - 35 mL/min
- Air - 350 mL/min
Signal - Signal A-Col Comp 1 or Signal A

9.3 Perform a blank column compensation run if necessary after the GC system stabilizes to establish the column bleed background which will be subtracted from all subsequent GC runs. Whenever conditions change or the system becomes contaminated it may be necessary to repeat this step to ensure a flat baseline for reliable integration.

9.4 Prepare calibration solutions according to Section 7.2.7.

9.5 Analyze each of the initial calibration standards and an instrument blank using the conditions in Section 9.2. Using the chromatography software, calculate the average response factors and %RSD.

9.6 Analyze a QCS sample immediately after each initial calibration. The RF for the QCS must be within 30% of the mean RF in the initial calibration. If the QCS sample fails, the cause must be determined and corrected before analysis of samples can proceed.

Note: Fuel standards from different sources may contain different compound mixes and therefore may not be reliable for verifying calibration standards.

9.7 If the initial calibration, the QCS, and the blank meet all the criteria specified in Sections 8.2 and 8.5 of this SOP, the remainder of the 12-hour analytical period may be used for the analysis of field and QC samples using the average RF from the initial calibration to quantitate the data.

9.8 Analyze a calibration verification standard and a quantitation limit verification once in every 12-hour analytical time period prior to an instrument blank analysis. The calibration verification check is performed in order to determine if the system is operating within the acceptable range as demonstrated by the percent difference meeting the appropriate QA/QC criteria. The quantitation limit verification insures the reported quantitation limit can be reliably achieved. The calibration verification is analyzed at 500 µg/mL and the quantitation limit verification at 50 µg/mL.

9.9 Sample analysis

Samples can be analyzed only after the initial calibration or calibration verification, QLS, LRB, and instrument blank meet all of the appropriate criteria specified in Section 8 of this SOP.

9.9.1 Set up a data acquisition sequence using the GC operating parameters in Section 9.2. The sample description shall include the client sample ID and the laboratory sample ID. Additional header information shall include the dilution factor, instrument ID, and the analyst's initials.

9.9.2 Include all QC sample extracts. It is highly recommended that the LRB, LFB and LFM/LFMD extracts be analyzed as early as possible in the analysis of a batch.

9.9.3 After completion of analysis, review the data to identify the fuel in the sample, or the carbon number range over which sample components elute. Compare the chromatographic pattern generated by analysis of the sample to the chromatographic pattern of fuels analyzed under the same conditions as the sample by electronically overlaying the chromatograms or by visually comparing printed chromatograms.

9.9.4 Review the baseline drawn by the data system integrator to verify that it accurately reflects the area response of the fuel in the sample. If, in the judgement of the analyst, it does not then draw a manual baseline from the point where the baseline starts to deviate from the trend to a second inflection point in the chromatogram, or to the end of the chromatogram if there is no second inflection point. See attachment D for examples. Document any manual integrations following the procedure described in Section 8.2.3 and Region 9 SOP #835.

9.9.5 Quantitate the data using the appropriate initial calibration mean RRF's for the identified fuel or for the carbon number range over which the sample components elute. Report sample results for all fuel types over which sample components elute, e.g. - diesel and oil range. If applicable, indicate degree of similarity of sample chromatogram to the fuel to which it is being compared. Print out quantitation reports and chromatograms for each field and QC sample.

9.9.5.1 Water calculations

Calculate results for target analytes using Equation 8:

EQ. 8

$$\text{Conc. } \mu g / L = \frac{A_x \times V_t \times DF}{RF \times V_o \times V_i}$$

where:

A_x	= area sum response of the sample
DF	= dilution factor
RF	= mean response factor from the initial calibration
V_o	= volume of water extracted in mL
V_i	= volume of extract injected in L
V_t	= volume of concentrated extract in L

9.9.5.2 Soil calculations

Calculate results for target analytes using Equation 9:

EQ. 9:

$$\text{Conc. ug / Kg (dry weight basis)} = \frac{A_x \times V_t \times DF}{RF \times W \times D \times V_i}$$

where:

A_x	= area sum response of the sample
D	= dry weight factor (Percent solids/100)
W	= weight of sample in grams
RF	= mean response factor from the initial calibration
V_t	= volume of concentrated extract in L
DF	= dilution factor
V_i	= volume of extract injected in L

9.9.6 Check the sample's surrogate recovery with the criteria in Section 8.6.

9.9.7 Diluted and re-analyze sample extracts if the area sum response exceeds the calibration range of the instrument. Dilute the extract so that the area sum response which was originally outside of the calibration range will fall within the upper half of the initial calibration range of the instrument.

9.10 The following are suggested remedial actions which may improve method performance; recalibration may be necessary after most of these actions:

9.10.1 Check and adjust GC operating conditions and temperature programming parameters.

9.10.2 Clean or replace the splitless injector liner. Use a new silanized liner.

9.10.3 Break off a short portion of the GC column from the end near the injector, or replace GC column. Breaking off a portion of the column will somewhat shorten the analyte retention times.

9.10.4 Prepare fresh calibration solutions and repeat the initial calibrations.

9.10.5 Replace any components in the GC that permit analytes to come in contact with hot metal surfaces.

10 DOCUMENTATION

10.1 Data from the Region 9 Laboratory is presented to the client in one of two general reporting formats: a complete data package which can be validated or a summary report data package. For the former the laboratory provides summary forms of calibration, quality control, and sample results along with the raw data for standards and field and QC samples, logbook pages, a report narrative, and an analytical report spreadsheet to the client. If a summary package is all that is required the laboratory provides a report narrative, analytical results spreadsheet, and sample specific raw data for delivery to the client and collects all other data included in a complete data package and files it at the laboratory. Section 10.2 details the requirements of a complete data package and Section 10.3 lists the summary report requirements.

10.2 Data package assembly.

The analyst, or other chemist, shall assemble a data package for each SDG in each case requiring the delivery of a complete data package according to the following instructions, and in the following order. Each section of the data package shall have a cover sheet titled with the appropriate section name. The data package shall be sequentially numbered after assembly using a hand operated numerator.

10.2.1 Report Narrative section.

10.2.1.1 The Report Narrative section shall contain a text narrative describing, but not limited to, the following.

10.2.1.1.1 Site name.

10.2.1.1.2 Case number.

10.2.1.1.3 SDG number.

10.2.1.1.4 Client sample ID - Laboratory sample ID cross reference

10.2.1.1.5 Date(s) the samples were received.

10.2.1.1.6 Protocol used to analyze the samples

10.2.1.1.7 LRB results

10.2.1.1.8 Surrogate recoveries

10.2.1.1.9 Internal standard recoveries.

10.2.1.1.10 LFM/LFMD results.

10.2.1.1.11 LFB results.

10.2.1.1.12 Analytical comments section to include:

10.2.1.1.12.1 Problems with analysis

10.2.1.1.12.2 Examples of calculations

10.2.2 Summary of Analytical Results spreadsheet

10.2.2.1 Include a spreadsheet containing a summary of the results for all target analytes for all samples and LRB's in the data package.

10.2.2.2 The header information for each sample contains the station location, Sample ID, and date sampled.

10.2.2.3 The results section contains the results for each target analyte as follows:

If an analyte is not detected then the quantitation limit with a "U" qualifier will be reported

If an analyte is detected then the value reported on the quant report and the associated qualifier (Section 10.2.5.1) will be reported.

If an analyte requires a dilution then value from the sample dilution will be reported.

10.2.3 Tracking Forms section.

The Tracking Form section shall contain the following forms.

10.2.3.1 A copy of the chain of custody record received with each sample shipment.

10.2.3.2 A copy of the shipper's airbill, or bill of lading.

10.2.4 QA/QC Summary section.

The QA/QC section contains all of the QA/QC summary forms for the specific sample delivery group. The forms are generated using macro driven spreadsheets. Check all of the forms to ensure that all of the filenames are correct, and that all of the appropriate standards, blanks, samples, and spikes have been included.

10.2.4.1 Surrogate recovery data.

10.2.4.2 LFB recovery data.

10.2.4.3 LFM/LFMD recovery data.

10.2.4.4 LRB summary data in chronological order.

10.2.4.5 Analytical sequence summary

10.2.5 Sample section.

The sample section contains the following forms and raw data for each sample in the data package, assembled in laboratory sample ID alphanumeric order.

10.2.5.1 Data report form listing all target fuels and the levels detected in the sample. Compare the form against the quantitation report to ensure that all detected fuels are reported. Also check to be sure that the appropriate qualifier appears on the form as indicated below.

B This analyte was detected in the associated method blank.

E The amount detected exceeds the calibration range of the instrument.

J The amount is only an estimated value.

U This compound was analyzed for, but not detected.

10.2.5.2 The raw data quantitation report of the data file.

10.2.5.3 The plotted chromatogram of the data file.

10.2.5.4 Documentation of any required manual integrations as described in Section 8.2.3 and EPA Region 9 SOP #835.

10.2.6 Standards section.

The Standards section contains the following forms and raw data for each initial calibration and each continuing calibration, in chronological order.

10.2.6.1 An initial calibration form containing the response factors for fuel in each calibration level, the average response factor for each fuel, and the percent RSD for each fuel in the initial calibration. Place the associated quantitation reports and chromatograms immediately following the form. Document any manual integrations following the procedure described in Section 8.2.3 and Region 9 SOP #835.

10.2.6.2 A continuing calibration form containing the average response factor for each fuel in the initial calibration, and the response factor and %D for each compound in the continuing calibration. Place the associated quantitation reports and chromatograms immediately following the form. Document any manual integrations following the procedure described in Section 8.2.3 and Region 9 SOP #835.

10.2.7 Raw QA/QC Data section.

The Raw QA/QC Data section contains the following forms and raw data.

10.2.7.1 For each LRB, submit the same data as that for each sample (Section 10.2.5).

10.2.7.2 For each LFB, LFM, and LFMD, submit the same data as that for each sample (Section 10.2.5).

10.2.8 Logbooks and Miscellaneous Data.

10.2.8.1 Copies of all instrument run logbook pages in chronological order by instrument.

10.2.8.2 Copies of all applicable standards preparation logbook pages.

10.2.8.3 Copies of all extraction logbook pages.

10.2.8.4 Copies of Percent Solids logbook pages, if applicable.

10.3 Summary Report and Raw Data

When the client requirements stipulate a summary report, prepare the report narrative, analytical results spreadsheet, and sample specific raw data and organizes other data associated with the package for filing in the event that future data review or validation is required.

10.3.1 Prepare the report narrative according to the requirements listed in Section 10.2.1.

10.3.2 Prepare the analytical results spreadsheet according to the specifications provided in Section 10.2.2.

10.3.3 Organize the raw data associated with the analysis of all the samples in the data package for filing and present it for review along with the report narrative and the spreadsheet. No summary forms need be generated with the raw data but any forms which would normally be generated as part of the analysis must be included in the package. For example, the calibration summary reports generated by the data system and used by the analyst to assess the acceptability of the calibration should be filed with the raw data.

10.3.3.1 Include sample tracking information as detailed in Section 10.2.3 as the analyst has a copy of the information readily available.

10.3.3.2 Sample raw data organized by Client sample ID must include: the quantitation report and the chromatogram.

10.3.3.3 Calibration data must include any available summary information and the quantitation reports and chromatograms for all initial calibrations and calibration verifications associated with the SDG. This information must be organized by instrument and date. Additionally, any manual integration must be demonstrated by including the associated peak integration.

10.3.3.4 Raw data for QC samples must be included. LRB, LFB, and LFM data should all be included in this order.

10.3.3.5 Runlogs and standard preparation logbooks need not be included in the raw data as these are already filed in an accessible manner in the laboratory.

10.4 Technical review.

Assign the data package an ESAT document control number after assembly. Each data package is reviewed by the team leader or a senior level chemist, other than the chemist who performed the analyses. All reviews are documented using the review form. After the peer review is performed, a cover letter is prepared and signed by the team leader. Final review of the data package is done by ESAT QA/QC Coordinator or ESAT Team Leader. The data package is then paginated and submitted to EPA Region 9.

10.5 Injection logbook.

Maintain a logbook for each instrument and record the filenumber, injection date, analyst, SDG, Case, Client Name, Lab Name, dilution, manual integration, and comments for each injection made.

10.6 Maintenance logbook

Maintain a logbook for each instrument. Record the date, the problem and resolution, and documentation of return to control. All preventive or routine maintenance procedures, as well as repairs or corrective or remedial actions must be documented.

10.7 Standards logbook

Maintain a logbook documenting the preparation of all standard solutions. Record the standard ID, preparation date, expiration date, solvent and solvent lot number used. Record the identification, supplier, lot number, concentration purity, and expiration date of the stock

standard solution used. Record the aliquot weight or volume of the stock standard solution, final volume of the standard solution and the concentration of the analyte(s) in the standard. Document the calculations used in preparing the standard.

11 REFERENCES

11.1 EPA Method 8015B, *Nonhalogenated Organics Using GC/FID*, Revision 2, Dec. 1996.

11.2 40 CFR, Part 136, Appendix B.

11.3 EPA Method 8000B, *Determinative Chromatographic Separations*, Revision 2, December, 1996.

11.4 EPA Region 9 SOP #835, *Chromatographic Integration Procedures*

11.5 EPA Region 9 SOP #805, *Refrigerator Temperature Monitoring*.

11.6 HP 5890 Gas Chromatograph Users Manual

11.7 EPA Region 9 SOP #125, *Disposal Procedures for Unused Aqueous Environmental Samples*

11.8 EPA Region 9 SOP #840, *Notebook Documentation and Control*

11.9 HP EnviroQuant Chemstation User's Guide

APPENDIX A

DEVIATIONS FROM METHOD 8015B

1. The applicability of this SOP has been extended to cover the determination of oil range hydrocarbons.

2. Calibration solutions are valid for six months from the date of preparation, or until ongoing QC results indicate a problem. There is no expiration time limit for standard solutions in the reference method.

3. The carbon number range used for Diesel in this SOP is from C_{12} to C_{26} instead of from C_{10} to C_{28} as in the reference method.

4. There is no requirement in the reference method to analyze or control on a quantitation limit standard (QLS).

5. Control limits for surrogate recovery are predetermined and neither obtained nor updated from the evaluation of laboratory data.

6. Control limits for LFB recovery are predetermined and neither obtained nor updated from the evaluation of laboratory data.

7. Control limits for LFM/LFMD recovery and RPD are predetermined and neither obtained nor updated from the evaluation of laboratory data.

8. This SOP allows for the re-analysis of certain standards, and QC and field samples if the first analysis exceeds QC criteria and the use of the results from the re-analysis instead of the first analysis in determining acceptance. This procedure is not addressed in the reference method.

9. This SOP requires that sample dilution be done so that the sample response in the diluted extract will fall within the upper half of the calibration range. This is not a requirement of the reference method.

Appendix B-2
1,4-Dioxane

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE #315

SEMIVOLATILE ORGANICS ANALYSIS

	Signature & Title	
Prepared by:	_____	_____
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Periodic Review:

Signature	Title	Date
_____	_____	_____
_____	_____	_____
_____	_____	_____

STANDARD OPERATING PROCEDURE #315

SEMIVOLATILE ORGANICS ANALYSIS

This SOP was prepared by ICF Consulting for the United States Environmental Protection Agency (USEPA) under the Environmental Services Assistance Team (ESAT) contract (EPA contract No. 68D60005).

APPROVED BY:

Ziyad Rajabi, Organic Group Leader	Date
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ESAT Document Control Number: B0101063-1371

TABLE OF CONTENTS

1 SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes the procedures used for the analysis of selected semivolatile organic compounds by Gas Chromatography/Mass Spectrometry (GC/MS) in extracts prepared from solid or liquid samples by EPA SW-846 extraction and cleanup methods appropriate to the analytes of interest. This SOP is based on procedures contained in EPA Method SW-846 8270.

The applicability of these procedures to specific project data quality objectives must be assessed on a case by case basis. The QC criteria specified in the procedures do not meet compliance criteria for either drinking water or NPDES monitoring projects.

2 METHOD SUMMARY

Sample extracts, which have been fortified with surrogate analytes and internal standards, are injected into a gas chromatograph with a Mass Spectrometer (MS). Analytes are separated in the narrow-bore fused-silica capillary gas chromatographic column during temperature programming, then detected by the MS.

Target semivolatile organic compounds are identified in the sample extract by comparing the mass spectra and GC retention times of the target analytes to the mass spectra and retention times of standards analyzed under the same conditions as samples. A response factor is established for each target and surrogate compound during the initial calibration by comparing the MS response of the quantitation ion produced by the target and surrogate compounds to the MS response for the quantitation ion produced by the associated internal standard. Each target analyte and surrogate are quantitated using an internal standard method of calculation using the average response factors from the initial calibration.

Non-target compounds are identified by comparing the resulting mass spectra of the non-target compound to the mass spectra contained in the National Institute of Standards and Technology (NIST) Library in the MS database. An estimated quantitation is performed for the non-target compounds by comparing the total MS response to the nearest internal standard total MS response, assuming a 1:1 response factor.

3 DEFINITIONS

3.1 Internal Standard (IS) - A pure analyte added to a sample, extract, or standard solution in a known amount and used to measure the relative responses of other method analytes and surrogates that are components of the same solution.

3.2 Surrogate Analyte (SA) - A pure analyte, which is extremely unlikely to be found in any sample, which is added to a sample aliquot in a known amount before extraction or other processing, and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

3.3 Laboratory Reagent Blank (LRB) - An aliquot of reagent water, sand, or sodium sulfate that is treated exactly as a sample including exposure to all glassware, equipment, solvents, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the solvents, or the equipment.

3.4 Laboratory Fortified Blank (LFB) - An aliquot of reagent water, sand, or sodium sulfate to which known quantities of the method analytes are added. The LFB is treated exactly as a sample. The LFB is used to determine whether the methodology is in control and to indicate the accuracy associated with laboratory procedures.

3.5 Laboratory Fortified Sample Matrix (LFM) and Laboratory Fortified Sample Matrix Duplicate (LFMD) - Two aliquots of the same sample to which known quantities of the method analytes are added. The LFM and LFMD are treated exactly as samples. The LFM and LFMD are used to determine whether the sample matrix contributes bias to sample results and to measure the precision associated with laboratory procedures

3.6 GC/MS Performance Check Solution (decafluorotriphenylphosphine (DFTPP) - A solution of DFTPP, 4,4'-DDT, pentachlorophenol, and benzidine used to evaluate the performance of the GC/MS system with respect to a defined set of method criteria.

3.7 Stock Standard Solution (SSS) - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials purchased from a commercial source.

3.8 Primary Dilution Standard Solution (PDS) - A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.9 Calibration Standard (CAL) - A solution prepared from the primary dilution standard or stock standard solution and the internal standard and surrogate analytes. The CAL solutions are used to calibrate instrument response with respect to analyte concentration

3.10 Quality Control Sample (QCS) – Equivalent to the mid-point initial calibration solution but prepared from a source different from the source of calibration standards. The QCS is used to check the accuracy of the initial calibration solutions.

3.11 Quantitation Limit Standard (QLS) - The lowest level CAL solution. The QLS is used to verify analytical system response at the quantitation limit.

3.12 System Performance Check Compounds (SPCC) - analytes that typically have low response factors. These compounds are used as indicators of deteriorating system performance.

3.13 Calibration Check Compounds (CCC) - analytes that may show high variability if there are system leaks or reactive sites on the column. These compounds are used as indicators of deteriorating system performance.

4 HEALTH & SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals should be minimized through the use of personal protective equipment and laboratory engineering and design. A reference file of material safety data sheets (MSDS) is available to all personnel involved in the chemical analysis and can be found in the library (Room 118) or Room 413.

4.2 Methylene chloride is a suspected carcinogen. Effects of overexposure: Acute inhalation or ingestion causes mild central nervous system depression. The primary toxic effect is narcosis. Other toxic effects are pulmonary edema, encephalopathy, and hemolysis. Methylene chloride irritates the eyes, skin, and respiratory tract. No systemic effects have been reported in humans, although excessive concentrations have caused cancer and liver and kidney damage in animals. Emergency and first aid - Inhalation: immediately remove to fresh air. If not breathing, administer mouth-to-mouth rescue breathing. If there is no pulse, administer cardiopulmonary resuscitation (CPR). Contact physician immediately. Eye contact: rinse with copious amounts of water for at least 15 minutes. Get emergency medical assistance. Skin contact: flush thoroughly for at least 15 minutes. Wash affected skin with soap and water. Remove contaminated clothing and shoes. Wash clothing before re-use, and discard contaminated shoes. Get emergency medical assistance. Ingestion: call local poison control

center for assistance. Contact physician immediately. Never induce vomiting or give anything by mouth to a victim unconscious or having convulsions.

4.3 Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Stock standard solutions of these compounds must be prepared in a fume hood. Routine procedures in this SOP do not require contact with concentrated solutions or neat materials. All standard preparation procedures associated with this SOP should be performed in a fume hood wearing protective clothing (lab coats) and safety glasses.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Sample extracts for GC/MS analysis are received from the extraction lab personnel and custody is transferred to the GC/MS laboratory staff. The GC/MS analyst acknowledges the receipt of the sample extracts by signing the appropriate sections in the extraction logbook. Copies of tracking sheets, chain-of-custody records, extraction logbook pages, and percent solids determination records should accompany the sample extracts.

5.2 The extracts are marked with the Region 9 Laboratory number, which can be checked against the tracking sheets and chain-of-custody record to determine the Client sample number, Case number, and Sample Delivery Group (SDG) number.

5.3 Store extracts in the refrigerator in Room 406 at 4 $\pm$ 2°C. Extracts must be analyzed within 40 days of extraction.

5.4 Store extracts in the refrigerator in Room 406 at 4 $\pm$ 2°C following analysis and submission of the data deliverables for an SDG an additional 90 days before segregating for disposal.

6 INTERFERENCES

6.1 Method interferences can be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus. Phthalates are commonly found as laboratory contaminants. The analytical system must be demonstrated to be free from interferences under the conditions of the analysis by running a laboratory reagent blank as described in Section 9. The use of non-polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components should be avoided.

6.2 Contamination by carryover can occur whenever high level and low level samples are sequentially analyzed. Splitless injection port liners must be cleaned carefully or replaced as

needed. After analysis of a sample containing high concentrations of compounds, a laboratory instrument blank should be analyzed to ensure that accurate values are obtained for the next sample.

6.3 It is important that samples and standards be contained in the same solvent, i.e., the solvent for final working standards must be the same as the final solvent used in sample preparation. If this is not the case, chromatographic comparability of standards to sample may be affected.

7 APPARATUS AND MATERIALS

7.1 GCMS System

7.1.1 Gas Chromatograph (GC): Hewlett Packard 5890 Series 2 or equivalent capable of multilevel temperature programming and constant carrier gas flow throughout the temperature range. The GC should be equipped with an automatic sample injector, splitless injection port, and Electronic Pressure Control (EPC).

7.1.2 GC column: 30 m, 0.25 mm ID, 0.25 m df, DB-5MS or equivalent. A fused silica capillary column with a bonded phase coating of 5% phenyl-95% methyl silicone such as DB-5, DB-5MS, Rtx-5, XTI-5, or HP-5. The use of a short (5 m) length of a deactivated, uncoated fused silica column (guard column) between the injection port and the analytical column, to trap nonvolatile extract residues, is optional.

7.1.3 Mass spectrometer: Hewlett Packard 5972 or equivalent. Capable of scanning from 35 to 500 amu every one second or less using 70 volts (nominal) electron energy in the electron impact ionization mode. Must be able to produce a mass spectrum that meets acceptance criteria when 50 ng of DFTPP is injected through the GC inlet.

7.1.4 Data system: HP EnviroQuant ChemStation G1701BA Version B.01.00 or equivalent. Able to control the GC/MS system and to acquire, store, and reduce mass spectral data. The software must be able to process any GC/MS data file by recognizing a GC peak within a retention time window, comparing the mass spectrum from the GC peak with spectral data in a data base, and generate a list of tentatively identified compounds with their retention times and scan numbers. The software must also allow integration of the ion abundance of any specific ion between specified time or scan number limits and to calculate response factors and concentrations of analytes in samples.

7.2 Standard solutions

Document the preparation of all standards in the Semivolatile Standards logbook following EPA Region 9 Laboratory SOP # 840, Notebook Documentation and Control.

7.2.1 Internal Standard Solution (IS) - A solution of acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, 1,4-dichlorobenzene-d_4, perylene-d_{12}, and naphthalene-d_8 at 2,000 μg/mL each in dichloromethane. Restek catalog # 31206 or equivalent.

7.2.2 Surrogate solution (SA) - A solution of 2-fluorobiphenyl, nitrobenzene-d_5, p-terphenyl-d_{14}, and 1,2-dichlorobenzene-d_4 (B/N surrogates) at 100 μg/mL each and 2-fluorophenol, phenol-d_5, 2,4,6-tribromophenol, and 2-chlorophenol-d_4 (Acid surrogates) at 150 μg/mL each in dichloromethane. Prepare by diluting purchased solutions - B/N surrogates: Restek catalog# 31002 or equivalent. Acid surrogates: Restek catalog# 31003 or equivalent.

7.2.3 Calibration Stock Standard. A solution of target analytes listed in Appendix B at a concentration of 2,000 μg/mL in dichloromethane. Restek SV calibration mix #2 (cat# 31008), #3 (cat# 31009), #4 (cat# 31010), #5 (cat# 31011), #7 (cat# 31013), and #8 (cat# 31026) or equivalent.

7.2.4 Calibration standards - A solution of target analytes listed in Appendix B at concentrations of 10, 25, 40, 60, and 80 μg/mL. Prepare by diluting from the calibration stock standard. Add 10 μL of the IS solution per 1.0 mL of standard.

7.2.5 GC/MS Performance Check Solution (DFTPP+). A solution of decafluorotriphenylphosphine (DFTPP), 4,4'-DDT, pentachlorophenol, and benzidine at 50 ng/μL each in methylene chloride. Prepare from a purchased solution - ULTRA Scientific cat# GCM-150 or equivalent.

7.2.6 Matrix Fortification Solution - A solution of 1,2,4-Trichlorobenzene, Acenaphthene, 2,4-Dinitrotoluene, Pyrene, n-Nitroso-di-n-propylamine, and 1,4-Dichlorobenzene (B/N spike mix) at 100 μg/mL each and Pentachlorophenol, Phenol, 2-Chlorophenol, 4-Chloro-3-methylphenol, and 4-Nitrophenol (Acid spike mix) at 150 μg/mL each in methanol. Prepare from purchased solutions - B/N spike mix: Restek catalog# 31004 or equivalent. Acid spike mix: Restek catalog# 31005 or equivalent.

7.2.7 Storage of Standard Solutions - Store the unopened ampulated stock standard solutions at 4 C (± 2 C). Store all other working standard solutions in glass bottles or vials with Teflon lined screw caps at -10 C and protect all standards from light.

Fresh standards should be prepared every six months, or sooner if comparison with check standards indicates a problem. The standard solution must be checked frequently for stability. Replace all working standard solutions after six months, or sooner if comparison with quality control check samples indicates a problem. CAUTION: Analysts must allow all standard solutions to equilibrate to room temperature before use.

7.2.8 Methylene chloride -- High purity pesticide quality or equivalent.

7.2.9 Helium carrier gas - as contaminant free as possible.

7.3 Syringes (10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, 1-mL).

8 QUALITY CONTROL

8.1 Quality control requirements include the initial demonstration of laboratory capability followed by regular analyses of laboratory reagent blanks, laboratory fortified blanks, and laboratory fortified matrix samples.

8.2 The laboratory must perform an initial demonstration of capability with each sample preparation technique used in analyzing analytes of interest with this SOP before analyzing any samples. See EPA Region 9 SOP #880, *Initial and Continuing Demonstration of Capabilities and Proficiency* for requirements and procedures.

8.2.1 Analyze Laboratory Fortified Blanks (LFBs) containing all the analytes of interest at a concentration of 40 µg/L in aqueous samples and 1320 µg/Kg in solid samples, equivalent to 40 µg/mL in the extract, to demonstrate initial laboratory capability.

8.2.2 Analyze LFBs which have been fortified with all analytes of interest at 10 µg/L in water samples and 330 µg/Kg in soil samples, corresponding to 10 µg/mL in the extract for MDL determination.

8.3 Mass calibration.

8.3.1 Calibrate the mass axis of the mass spectrometer daily. You must also calibrate the mass axis whenever the mass spectrometer is shut down, or whenever there is a mass mis-assignment. Mass calibration is performed to ensure the accurate assignment of masses to ions generated in the ion volume of the mass spectrometer.

Perfluorotributylamine (FC43) is used to perform calibration of the mass axis. The FC43 spectrum with the following criteria are recommended:

Mass	Target % of Mass 69
69	100
131	25.0 - 40.0
219	25.0 - 40.0
414	1.4 - 4.0
502	0.5 - 2.0

8.3.2 Take corrective action if the FC43 spectrum does not meet the criteria listed above as DFTPP will probably not pass criteria. The corrective action may be as simple as adjusting the mass gain and peak width or manually retuning the MS. Alternatively, retuning the MS by selecting target tune with mass ratio(s) set based on the failure on criteria in Section 8.4.4. If retuning the MS does not produce adequate FC43 spectra or repeated failure to meet DFTPP criteria, further maintenance such as cleaning the ion source may be required. See Section 9.4.

8.4 GC/MS System Performance Check

8.4.1 Prior to the analysis of any calibration standards, blanks, and samples (including LFM/LFMDs), the GC/MS system must meet the mass spectral ion abundance criteria for DFTPP. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target and non-target compounds.

8.4.2 Frequency of GC/MS Performance Check.

8.4.2.1 Analyze the DFTPP solution once at the beginning of each 12-hour period during which standards, blanks and samples are to be analyzed. The twelve-hour time period begins at the moment of injection of the DFTPP solution. The time period ends after twelve hours have elapsed. If a sample is injected after the 12-hour time period has elapsed it must be re-analyzed.

8.4.3 Analyze the DFTPP solution according to Section 9 of this SOP.

8.4.4 The ion abundance ratios must meet the following criteria:

Mass (m/z)	Relative Ion Abundance Criteria
51	30 - 60% of the base peak
68	less than 2% of mass 69
70	less than 2% of mass 69
127	40 -60% of the base peak
197	less than 1% of mass 198
198	Base peak (100% relative abundance)
199	5 - 9% of mass 198
275	10 - 30% of the base peak
365	Greater than 1% of the base peak
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17 - 23% of mass 442

8.4.4.1 If the ion abundances fail to meet the criteria listed above the DFTPP chromatogram should be examined for any obvious chromatographic problems (e.g., bad injection leading to poor response etc.) If the problem is determined to be related to poor chromatography, take the necessary corrective action and re-analyze the DFTPP. If the DFTPP continues to fail the ion abundance criteria, retune the mass spectrometer. It may also be necessary to clean the ion source or take other corrective action to achieve the ion abundance criteria. See Section 9.4.

8.4.4.2 Evaluate the breakdown of DDT using Equation 1. Locate the degradation products of 4,4'-DDT (4,4'-DDD and 4,4'-DDE). If the percent breakdown calculated using peak areas based on each Quantitation ion (Qion) exceeds 20%, corrective maintenance must be taken

Equation 1:

$$\%\ 4,4'\text{-DDT Breakdown} = \frac{\text{Total Qion Area (DDE + DDD)}}{\text{Total Qion Area (DDE + DDD + DDT)}} \times 100$$

Qions of DDE: 246 dalton, DDD: 235 dalton, DDT: 235 dalton

8.4.4.3 Benzidine and pentachlorophenol responses should be at their expected levels in the DFTPP solution and peak tailing should be minimal. Replacing the inlet

liner and /or the inlet seal and breaking off a portion of the column from the injector end should restore instrument performance.

8.5 Initial calibration.

8.5.1 Calibrate the GC/MS system whenever corrective action which may change instrument response (e.g., ion source cleaning, column replacement, etc.) is performed or if the continuing calibration acceptance criteria have not been met.

8.5.2 Analyze the 10 or 25 μg/mL calibration standard according to Section 9.

8.5.2.1 Evaluate the separations of anthracene /phenanthrene and benzo(a)anthracene/chrysene. Anthracene /phenanthrene should have baseline separation. Benzo(a)anthracene/chrysene should be separated by a valley whose height is less than 25% of the average height of the two peaks. If not, the GC column requires maintenance.

8.5.2.2 If any target analytes, surrogates or internal standards are mis-identified or not found, corrective action or system maintenance is required.

8.5.3 If all performance criteria are met, analyze the remaining initial calibration standards according to Section 9 of this SOP.

8.5.4 The data system calculates the relative response factor (RRF) for each target compound and surrogate for all five calibration standards using Equation 2. The quantitation ions and internal standard assignments are listed in Appendix C.

Equation 2:

$$RRF = \frac{A_x \times C_{is}}{A_{is} \times C_x}$$

Where

A_x = Area of quantitation ion of compound x
A_{is} = Area of quantitation ion for associated internal standard
C_x = Concentration of compound x in μg/mL
C_{is} = Concentration of the associated internal standard in μg/mL

8.5.5 Calculate the average RRF for all analytes

8.5.6 Calculate the percent relative standard deviation (%RSD) of the RRF values for each compound using Equation 3.

Equation 3

$$\%RSD = (SD/ RRF_{avg})\times 100$$

$$SD \sqrt{\frac{\sum_{i\ 1}^{n} (x_i\ x_{ave})^2}{n\ 1}}$$

8.5.7 Check the initial calibration for misidentified peaks due to retention time shifts. The most commonly mis-assigned compounds are the 1,3- and 1,4-dichlorobenzenes and the benzo(b) and benzo(k) fluoranthenes.

8.5.8 Verify that the minimum average RRF's in the initial calibration for the following system performance check compounds (SPCC's) is 0.050:

N-nitroso-di-n-propylamine
hexachlorocyclopentadiene
2,4-dinitrophenol
4-nitrophenol

Corrective action must be taken before sample analysis can begin if any SPCC fails the minimum RRF criterion.

8.5.9 All other analytes must meet the minimum RRF criteria in Appendix C.

8.5.10 Verify that the maximum %RSD for the following calibration check compounds (CCC's) in the initial calibration is 20:

acenaphthene	4-chloro-3-methylphenol
1,4-dichlorobenzene	2,4-dichlorophenol
hexachlorobutadiene	2-nitrophenol
di-n-octyl phthalate	phenol
fluoranthene	pentachlorophenol
benzo(a)pyrene	2,4,6-trichlorophenol

Corrective action must be taken before sample analysis can begin if any CCC fails the maximum %RSD criterion.

8.5.11 All other analytes should meet the maximum %RSD of 20. Any project specific analyte of interest must meet the maximum %RSD criterion. If one or more analytes exceed the RSD limit, the initial calibration may still be acceptable if the following conditions are met:

8.5.11.1 The %RSD of the analytes that exceed the limit is 30.

8.5.11.2 The mean of the RSD values for all analytes is less than or equal to 20%.

8.5.11.3 If an analyte that exceeds the %RSD limit is found in a sample extract, that extract must be re-analyzed using an initial calibration that meets QC limits for that analyte.

8.5.12 If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the failed one in the ICAL. If more than one standard fails, corrective action is required before sample analysis begins.

8.5.13 If the five point calibration fails the minimum RRF or maximum %RSD criteria for target analytes with on column quantitation limits of 25 ng listed in Appendix D, then a four-point calibration, excluding the 10 μg/mL standard, may be used if it meets the initial calibration criteria.

8.5.14 Remember that the lowest concentration standard defines the reporting limit for each compound. If appropriate reporting limits cannot be obtained by this procedure, the system must be repaired so that the criteria are satisfied before any samples are analyzed. If repairs are made to the system, then a new initial calibration must be performed.

8.5.15 No quantitation ion may saturate the detector.

8.5.16 Analyze a QCS sample immediately after each initial calibration. The RRF for each analyte in the QCS must be within 30% of the mean RRF in the initial calibration. If the QCS sample fails, the cause must be determined and corrected before analysis of samples can proceed.

8.5.17 If the initial calibration and the QCS meet the specified criteria, the remainder of the 12-hour analytical period may be used for the analysis of field and QC samples, using the average RRF from the initial calibration to quantitate the sample data.

8.5.18 Manual integration. There will be instances when the data system will not produce accurate integrations. Examples of this are misidentification of a peak, inaccurate dropping of a perpendicular between peaks, or failure to integrate the entire tail of a peak. When necessary, chromatograms can be manually integrated if the following steps are taken (see SOP 835, *Chromatographic Integration Procedures*):

8.5.18.1 Print a view of the chromatogram to be reintegrated using QEDIT. Include the background-subtracted spectrum of the apex of the peak and the reference spectrum. Indicate the reasons for manually integrating the chromatographic results on the chromatogram and initial and date the statement.

8.5.18.2 Reintegrate the peak and print the new view. Save the reintegrated value(s). Print the peak and reference spectra. Document the manual integration on the reintegrated chromatogram and initial and date the statement.

8.5.18.3 Print the new quant report and chromatogram after all manual integrations have been completed. Indicate each manual integration on the new quant report. Document the fact that there was manual integration in the instrument's run log and initial and date the statement.

8.5.18.4 Show the chromatograms, quant reports and log book to a supervisor, QA/QC coordinator or team leader for review and acceptance. The QA/QC coordinator or team leader will initial and date the integrations.

8.6 Calibration Verification

8.6.1 Verify the MS tune and initial calibration at the beginning of each 12-hour period (see Section 8.4.2.1 for definition of 12-hour time period) when analyses of field and QC samples are performed using the following procedure.

8.6.2 Analyze a DFTPP+ solution according to Section 9

8.6.2.1 Check that the DFTPP ion abundances meet the criteria in Section 8.4.4

8.6.2.2 Evaluate the DDT breakdown using the Equation 1 and the acceptance criteria in Section 8.4.4.2.

8.6.2.3 Evaluate the benzidine and pentachlorophenol responses according to the criteria in section 8.4.4.3.

8.6.3 Analyze the calibration verification standard (25 μg/mL) according to Section 9 of this SOP.

8.6.4 The responses of the internal standards in the calibration verification standard must meet the criteria in Section 8.11.2.

8.6.5 Check the calibration verification for misidentified peaks due to retention time shifts. The most commonly mis-assigned compounds are closely eluting pairs such as the benzo(b) and benzo(k)fluoranthenes. If any are found, corrective action must be taken and the chromatogram re-quantitated to ensure the corrective action was successful.

8.6.6 Calculate the relative response factor (RRF) for each target compound and surrogate using Equation 1. The quantitation ions and internal standard assignments are listed in Appendix C.

8.6.7 Calculate the percent difference (%D) between the continuing calibration RRF's and the average RRF's from the most recent initial calibration for each target compound and surrogate using Equation 4.

Equation 4

$$\%D = \frac{RRF_c - \text{avg } RRF_i}{\text{avg } RRF_i} \times 100$$

Where :

RRFc = relative response in the continuing calibration
Avg RRFi = average relative response in the initial calibration

8.6.8 Verify that the minimum RRF for the SPCC's listed in section 8.5.8 is 0.050.

8.6.9 All other analytes must meet the minimum RRF's listed in Appendix B.

8.6.10 Verify that the maximum %D for the CCC's listed in section 8.5.10 is 25.

8.6.11 All other analytes must meet the maximum %D criteria listed in Appendix B.

8.6.12 All project specific analytes of interest must meet the minimum RRF and maximum %D criteria in Appendix B. If one or more analytes exceed the minimum RRF and maximum %D limit, the calibration verification may still be acceptable if the following conditions are met:

8.6.12.1 The %D of the analytes that exceed the limit is 40.

8.6.12.2 The minimum RRF of the analytes that exceed the limit is 0.050.

8.6.12.3 The mean of the %D values for all analytes is less than or equal to 25.

8.6.12.4 If an analyte that exceeds the QC limits is found in a sample extract, that extract must be re-analyzed using a calibration verification that meets QC limits for that analyte.

8.6.13 If any of the criteria are not satisfied a second continuing calibration may be analyzed. Repeated failure requires the analysis of a new initial calibration before analysis of samples can begin. If repairs to the system are required then a new initial calibration must be performed.

8.6.14 The analyst should observe trends in the data such as declining response, erratic relative response, loss of classes of compounds, etc. which may signal the need for instrument maintenance. See Section 9.4.

8.7 Quantitation Limit Standard analysis

8.7.1 Analyze a quantitation limit standard (QLS) in each 12-hour period (see Section 8.4.2.1 for definition of 12-hour time period) when analyses of field or QC samples are performed. The QLS is used to verify analytical system response at the quantitation limit.

8.7.2 Analyze the 10 μg/mL calibration standard according to Section 9 of this SOP

8.7.3 Calculate the percent of true value for each target compound using Equation 5.

Equation 5

$$\% \text{ True Value} = (Cd / Tv) \times 100$$

Where:

Cd = Concentration determined by analysis
Tv = True value

8.7.4 The accuracy for each analyte, expressed as a percentage of true value must be between 50 - 150%. If the QLS sample fails, the cause must be determined and corrected before analysis of samples can begin.

8.7.5 If the 10 µg/mL QLS standard fails for target analytes with on column quantitation limits of 25 ng listed in Appendix B, then analyze a 25 µg/mL standard. Calculate the % True Value using Equation 6. The %True Value must be between 50 - 150%. If the QLS sample fails, the cause must be determined and corrected before analysis of samples can begin.

8.7.6 If the QLS standard fails, a fresh QLS solution of that standard may be analyzed.

8.8 Laboratory Reagent Blank (LRB) analysis.

8.8.1 An LRB is extracted with each extraction batch in order to demonstrate that the entire analytical system - from extraction through GC/MS analysis - is free of contamination.

8.8.2 Analyze the LRB according to Section 9 of this SOP.

8.8.3 Evaluate the LRB as soon as possible after it has been analyzed to determine if the following criteria have been met:

The LRB is acceptable if it contains less than the quantitation limit (QL) of any single target compound. Exceptions are the target phthalate esters, each of which may be present at up to five times the QL.

8.8.4 The LRB internal standards must meet the criteria listed in Section 8.11.2

8.8.5 The LRB surrogate recoveries must meet the criteria listed in Section 8.12.1

8.8.6 Corrective action - If the LRB is not acceptable, the source of the contamination must be found and eliminated and the problem documented before analysis can proceed. If re-analysis does not solve the problem, the batch may have to be re-extracted. Corrective action is decided by the EPA TOPO on a case by case basis.

8.8.7 If surrogate or internal standard recoveries do not meet acceptance criteria, re-analyze the extract. If the surrogate recoveries still do not meet acceptance criteria, document failure in the report narrative.

8.9 Laboratory fortified matrix and duplicate analysis.

8.9.1 A laboratory fortified matrix and a duplicate sample are extracted and analyzed for each batch of twenty or fewer samples extracted as a group.

8.9.2 LFM and LFMD extracts should be analyzed as soon as possible following the analysis of the sample designated as the laboratory fortified matrix sample.

8.9.3 Analyze the LFM and LFMD according to Section 9 of this SOP.

8.9.4 The recovery and RPD criteria for the LFM and LFMD analyses are as follows:

	%Recovery		**RPD**	
Compound	**Water**	**Soil**	**Water**	**Soil**
Phenol	12 - 110	26 - 100	21	35
2-Chlorophenol	27 - 123	25 - 102	16	50
1,4-Dichlorobenzene	36 - 100	28 - 104	22	27
n-Nitroso-di-n-propylamine	41 - 116	41 - 126	38	38
1,2,4-Trichlorobenzene	39 - 100	38 - 107	28	23
4-Chloro-3-methylphenol	23 - 100	26 - 103	42	33
Acenaphthene	46 -118	31 - 137	31	19
2,4-Dinitrotoluene	24 - 100	28 - 100	38	50
4-Nitrophenol	10 - 100	11 - 114	50	47
Pentachlorophenol	9 - 103	17 - 109	50	107
Pyrene	26 - 127	35 - 142	31	36

8.9.5 Calculate the recovery of each compound using Equation 6.

Equation 6

$$\% \text{ Rec} = ((SSR - SR)/SA) \times 100$$

where,

SSR = Spiked sample result (volume/weight corrected)
SR = Sample result (volume/weight corrected)
SA = Spike added

8.9.6 Calculate the relative percent differences (RPD) of the recoveries of each compound in the matrix spike and matrix spike duplicate using Equation 7.

Equation 7

$$RPD = \frac{(LFMC - LFMDC)}{(LFMC + LFMDC)/2} \times 100$$

where:

LFMC = Measured concentration of analyte in LFM
LFMDC = Measured concentration of analyte in LFMD

8.9.7 The limits for LFM/LFMD recovery are advisory limits only. If the limits are not met, then no further action is required, as long as the LFB is within limits, since the purpose of these analyses is to determine matrix effects on compound recovery. However, frequent failure to meet the recovery or RPD criteria should alert the analyst that a problem may exist and must be investigated. The analyst should analyze the matrix spike solution and check the recoveries of the spike compounds. A new solution should be prepared if the recoveries are not within 30% of the expected values.

8.10 Laboratory Fortified Blank (LFB) An LFB is analyzed to demonstrate that the analytical system is in control. The LFB is extracted and analyzed once per batch or every 20 samples, whichever is more frequent. The LFB is an LRB spiked with laboratory fortified matrix solution.

8.10.1 All analytes and surrogates must be recovered within the QC limits listed in section 8.9.4. If not, the source of the problem must be determined prior to reporting any sample data. It usually indicates either a discrepancy between the spiking solution and the calibration standard, or a problem in the extraction laboratory.

8.10.2 The table below lists the action to be taken based on the LFB and LFM/LFMD results.

QC ACCEPTANCE MATRIX

+ = PASS = FAIL

CASE	1	2	3	4	5	6	7	8
LFB - % REC	+	+	+	+				
LFM/LFMD -% REC	+	+	+		+		+	
LFM/LFMD - RPD	+	+			+	+		

Case 1: Extraction batch is acceptable.

Case 2: Extraction batch is acceptable; matrix effect confirmed.

Cases 3 & 4: Extraction batch is unsatisfactory. Investigate LFM/LFMD problem and document findings in report narrative.

Case 5: Extraction batch is rejected. The batch may have to be re-extracted unless LFB problem is determined and documented.

Cases 6, 7 & 8: Extraction batch is rejected. Re-extract batch.

8.11 Internal standard recovery.

8.11.1 Check the internal standard recovery, determined by total area, for all standards, blanks, samples, and spikes immediately after analysis in order to determine if all applicable criteria have been met.

8.11.2 If the total area of any internal standard in any blank, sample, or spike analysis changes by more than a factor of two (-50% to +100%) of the corresponding internal standard from the preceding 12-hour calibration standard, the system must be checked for malfunctions and the necessary corrections made (see Section 9.4). After the corrections are made, the analyses performed while the system was not in control must be repeated. Keep in mind that many "corrections" to the system will require a new initial calibration be performed prior to re-analysis of the samples.

8.11.3 If after re-analysis, the total areas for all internal standards are within the criteria, then the problem is considered to have been within the laboratory's control. Report the results from the re-analysis and submit the data for both analyses. Distinguish between the analysis and re-analysis by adding an "RI" suffix to the client sample ID on the re-analysis. The problem must be documented in the report narrative (see Section 10.2.1.1).

8.11.4 If re-analysis of the sample does not solve the problem, report the results from the first analysis and submit the data from both analyses. Distinguish between the analysis and re-analysis by adding an "RI" suffix to the client sample ID on the re-analysis. The problem must be documented in the report narrative (see Section 10.2.1.1).

8.11.5 Check internal standard retention times in all standards immediately after data acquisition. If the retention time for any internal standard changes by more than 0.2

minute from the latest daily calibration standard, the system must be inspected for malfunctions, and the necessary corrections made. Compare the IS retention times in field and QC samples analyzed within the 12-hour analytical period of the initial calibration to the IS retention times in the 25 μg/L standard.

8.12 Surrogate recovery.

8.12.1 Calculate the surrogate recovery in all blanks, samples, and spike immediately after analysis using Equation 8 and compare to the following criteria.

Compound	**Water %R**	**Soil %R**	
2-Fluorophenol	21 - 110	25 - 121	
Phenol-d5	10 - 110	24 - 113	
Nitrobenzene-d5	35 - 114	23 - 120	
2-Fluorobiphenyl	43 - 116	30 - 115	
2,4,6-Tribromophenol	10 - 123	19 - 122	
Terphenyl-d14	33 - 141	18 - 137	
2-Chlorophenol-d4	33 - 110	20 - 130	(advisory)
1,2-Dichlorobenzene-d4	16 - 110	20 - 130	(advisory)

Equation 8

$$\%R = (\text{Amount Found}/\text{Amount Spiked}) \times 100$$

8.12.2 Take the following steps if the recovery of one or more of the surrogates is not within the limits.

8.12.2.1 Check to ensure that there are no calculation errors, and check the system performance.

8.12.2.2 Re-analyze the extract if a system performance problem or calculation error is not evident. The extract may be diluted for re-analysis if examination of the chromatogram so indicates (e.g., very large amounts of hydrocarbon).

8.12.2.3 If re-analysis of the extract does not solve the problem, the sample may have to be re-extracted. Corrective action is decided by the EPA TOPO on a case by case basis.

8.12.2.4 Do not re-extract undiluted samples with surrogate recoveries outside the limits if the diluted analysis with acceptable surrogate recoveries is being submitted. Report the event in the run log and report narrative.

8.12.2.5 Do not re-analyze the LFM or LFMD samples, even if the surrogates recoveries are outside the limits.

8.12.2.6 If the sample associated with the LFM/LFMD analyses does not meet the surrogate recovery criteria, it should be re analyzed only if the matrix spike and duplicate surrogate recoveries are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need re-analysis. The similarity in surrogate recoveries in the sample and spike analyses must be discussed in the report narrative (See Section 10.2.1.1).

8.12.3 If the surrogate recoveries of the re-analysis of the extract are within limits, then:

8.12.3.1 If the re-analysis was undiluted, the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses. Distinguish between the analysis and re-analysis by adding an "RE" suffix to the client sample ID on the re-analysis. The problem must be documented in the report narrative (see Section 10.2.1.1).

8.12.3.2 If the re-analysis was diluted, the problem was a matrix effect. Report the results from the re-analysis and submit the data from both analyses and discuss the result in the report narrative. Distinguish between the undiluted and diluted analysis by adding a "DL" suffix to the client sample ID on the diluted analysis. The problem must be documented in the report narrative (see Section 10.2.1.1).

8.12.4 If the sample was re-extracted and the surrogate recoveries of the re-extraction are within limits, then the problem was within the laboratory's control. Report the results from the re-extraction. Distinguish between the original analysis and the re-analysis by adding the "RE" suffix to the client sample ID in the re-analysis. The problem must be documented in the report narrative (see Section 10.2.1.1).

8.12.5 If the re-extraction does not solve the problem, report the results from the first analysis and submit the data from both analyses. Distinguish between the original analysis and

the re-analysis by adding the "RX" suffix to the client sample ID in the re-analysis. The problem must be documented in the report narrative (see Section 10.2.1.1).

8.13 Sample dilution.

8.13.1 Dilute and inject a new aliquot of the extract if the on-column concentration of any target compound in any sample exceeds the initial calibration range. Add more internal standard solution to the diluted extract to maintain the initial internal standard concentration. Use the following criteria in performing dilutions:

8.13.1.1 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

8.13.1.2 Keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument by choosing an appropriate dilution factor.

8.13.1.3 Do not dilute LFM/LFMD samples to get either the spiked or non-spiked target compounds within the initial calibration range. If the sample from which the spike aliquots were taken contains high levels of the spiked analytes, calculate the concentration and recovery of the analytes from the undiluted analysis, and note the problem in the report narrative.

8.13.1.4 In the case of extremely contaminated samples several dilutions may be required.

8.13.1.5 Distinguish between the undiluted and diluted analysis by adding a "DL" suffix to the client sample ID on the diluted analysis.

8.13.2 Demonstrate that there is no carryover to subsequent analyses after a sample is analyzed that contains one or more target compounds at a level exceeding the initial calibration range of the system. This can be done by analyzing an instrument blank.

8.13.2.1 Monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample that exceeded the limits above. The maximum contamination criteria are as follows:

8.13.2.2 The sample should not contain a concentration above the QL for the target compounds that exceeded the limits in the contaminated sample, unless other analytes present in the ample indicate that the presence of these compounds is likely. The most common scenario for this is when PNAs are found in both samples, and the pattern in the second sample does not follow the pattern in the first.

8.13.3 The most common cause of a carryover is hydrocarbon in the oil/asphalt range. This may require cleaning the injection port and analyzing an instrument blank.

8.14 Review of Target Analytes

Review each reported value for both qualitative and quantitative validity. This process, in particular the qualitative review of mass spectra, relies upon the technical judgement of the analyst.

8.14.1 Qualitative Review

Both the relative retention time and the mass spectra must match those of the standard's in order for a target compound to be identified as present in a sample.

8.14.1.1 Target analytes must elute within 0.06 relative retention time units of the analyte in the continuing calibration standard. The relative retention time is the retention time of the target divided by the retention time of the associated internal standard. If the relative retention time for the target analyte in the CCAL is 0.82 then the peak in the sample must have a relative retention time of 0.76 to 0.88.

8.14.1.2 The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other.

8.14.1.3 The mass spectra used for qualitative identification must be obtained using the GCMS system used to analyze the samples.

8.14.1.3.1 All ions present in the standard mass spectra at a relative intensity of 10 percent of the most abundant ion must be present in the sample spectra.

8.14.1.3.2 The relative intensities of the ions must agree within ±30 % (absolute) between the standard and sample spectra.

8.14.1.3.3 Ions present in the sample at greater than 10 percent abundance but not present in the standard spectra must be reviewed and accounted for by the analyst making the comparison.

8.14.1.3.4 If a compound cannot be verified by these criteria but, in the technical judgement of the analyst, is present the supporting evidence must be indicated on the raw data and the analyte reported.

8.14.2 Quantitative Review

Review reported values to determine that the correct calculations were used to generate the results, that the RRFs from the associated continuing calibration standard were used, and that all other numbers are accurate.

8.14.2.1 Review of data system integrations

The analyst must review the data system integration to verify that the internal standards, surrogates and target compounds are integrated properly. In the event that the analyst observes an incorrect integration, the analyst must manually correct the integration and document the correction following Section 8.5.11 of this SOP and EPA Region 9 SOP #835, *Chromatographic Integration Procedures.*

8.14.2.2 Water calculations

Calculate results for target analytes using Equation 9:

Equation 9:

$$\text{Conc. } \mu g / L = \frac{A_x \times C_{is} \times V_t \times V_i \times DF}{A_{is} \times \overline{RRF} \times V_o}$$

where:

A_x = area of the quantitation ion of the compound
C_{IS} = concentration of internal standard in μg/mL (normally 20)
DF = dilution factor
A_iS = area of the quantitation ion of the associated internal standard
RRF = analyte's mean relative response factor from the initial calibration
V_o = volume of water extracted in mL

V_i = volume of extract injected in μL
V_t = volume of concentrated extract in μL

8.14.2.3 Soil calculations

Calculate results for target analytes using Equation 10:

Equation 10:

$$\text{Conc. ug / Kg (dry weight basis)} = \frac{A_x \times C_{is} \times V_t \times V_i \times DF \times GPC}{A_{is} \times \overline{RRF} \times W \times D}$$

where:
A_x = area of the quantitation ion of the compound
C_{IS} = concentration of Internal Standard in μg/mL (normally 20)
D = dry weight factor (Percent solids/100)
W = weight of sample in grams
A_{IS} = area of the characteristic ion of the associated internal standard
RRF = analyte's mean relative response factor from the initial calibration
V_t = volume of concentrated extract in μL
DF = dilution factor
GPC = GPC factor, normally 1.0 if not used, 2.0 if used
V_i = volume of extract injected in μL

8.15 Review the Tentatively Identified Compound search results for the following:

8.15.1 Verify that all unknown peaks in the chromatogram greater than10 percent of the area of the nearest internal standard are accounted for in the summary.

8.15.2 Relative intensities of the major ions in the NIST reference spectrum (ions greater than 10 percent of the most abundant ion) should be present in the sample.

8.15.3 The relative intensities of the major ions should agree within 20 percent.

8.15.4 Molecular ions present in the reference spectrum should be present in the sample spectrum.

8.15.5 Ions present in the sample spectrum but not in the reference spectrum shall be reviewed for possible background contamination or the presence of co-eluting compounds.

8.15.6 Ions present in the reference spectrum but not within the scan range (35 to 500 amu) of the method should not be considered when making a tentative identification.

8.15.7 If, in the technical judgement of the analyst, no valid tentative identification of the compound can be made, the compound should be reported as "Unknown". The analyst shall attempt classification of the unknown compound (i.e., unknown hydrocarbon, unknown aromatic, unknown chlorinated compound, etc.). The probable molecular weight should be included, if distinguishable.

8.16 If any of the data reports have been edited, or if manual integration or quantitation has been performed, the analyst must identify the changes. A supervisor, QA/QC coordinator, or team leader must review both the original and the changed data and indicate acceptance by initialing and dating the report. See SOP#835, *Chromatographic Integration Procedures.*

9 ANALYTICAL PROCEDURES

9.1 Analytical system preparation.

9.1.1 Calibrate the mass axis and optimize the peak width of the mass spectrometer using FC43 at the beginning of each 12-hour period during which standards or QC or field samples are to be analyzed.

9.1.2 Check the GC/MS system for leaks prior to the analysis of the DFTPP tuning compound. The system must also be checked for leaks after any disconnection and re-connection in the entire system, from the carrier gas source to the MS.

9.1.2.1 Acquire a scan of m/z's 18, 28, and 69. Observe the ratio of the water peak (m/z 18) to the nitrogen peak (m/z 28). If a leak is present in the mass spectrometer, the nitrogen peak will be greater than the water peak. Corrective action must be taken if a leak is detected. The ratios of these ions to the m/z 69 ion should be no more than 10%. Ratios between 10 and 20% indicate a problem that should be repaired as soon as practical, and ratios greater than 20% indicate problems that should be repaired immediately.

9.1.3 The GC/MS system must meet the mass spectral ion abundance criteria for DFTPP and the maximum breakdown criteria for DDT prescribed in Section 8.4 prior to the analysis of any calibration standards, blanks, or samples

9.1.3.1 Analyze the DFTPP+ solution using the system conditions in Appendix E. Obtain ion abundance ratios from a background subtracted average of three scans around the apex of the DFTPP peak or from any one or two of these scans with or without background subtraction. The ion abundance ratios must meet the criteria listed in Section 8.4.4. If not, appropriate corrective action must be taken before calibrations or extracts are analyzed. See Section 9.4.

9.1.3.2 Evaluate the percentage of DDT breakdown as described in Section 8.4.4.2. If it is greater than 20%, take corrective action.

9.2 Calibration - The target compounds for this method are listed in Appendix B.

9.2.1 Five-point initial calibration

Perform a five-point initial calibration in order to demonstrate that the GC/MS system provides a linear response over the desired concentration range.

9.2.1.1 Create a method (if not present already) to operate the GC and collect data as described in Appendix E. Create a sequence to use this method to analyze the standard solutions - 80, 60, 40, 25 and 10 μg/mL.

9.2.1.2 Analyze the 10 or 25 μg/mL standard. Verify that all of the peaks have been properly identified. Update the retention times in the method. Save the method and re-quantitate the chromatogram. Make sure that all of the standards are quantitated using the updated retention times.

9.2.1.3 Update the initial calibration response factors in the method by associating the correct data file with each calibration level. Save the method.

9.2.1.4 Generate the initial calibration summary report. Samples shall not be analyzed if the initial calibration does not meet the criteria specified in Appendix B of this SOP.

9.2.1.5 Analyze a QCS sample immediately after each initial calibration. The RRF for each analyte in the QCS must be within 30% of the mean RRF in the initial calibration. If the QCS sample fails, the cause must be determined and corrected before analysis of samples can proceed.

9.2.1.6 If the initial calibration and the QCS meet all the criteria specified in Section 8.5 of this SOP, the remainder of the 12-hour analytical period may be used for the analysis of blanks, spikes and samples, using the average RRF from the initial calibration to quantitate these data files.

9.2.2 Calibration Verification

Analyze a calibration verification standard once in every 12-hour analytical time period, after DFTPP tuning and prior to continuing with extract analysis. The calibration verification is performed in order to determine if the GC/MS system is operating within the acceptable range as demonstrated by the percent difference and the minimum response factor criteria meeting the appropriate QA/QC criteria. The continuing calibration is analyzed at a level of 25 µg/mL.

9.2.2.1 Analyze the 25 µg/mL standard. Verify that all compounds have been properly identified. Update the retention times in the method. Save the method. Re-quantitate the chromatogram, again verify that all compounds have been properly identified. Select Report Continuing Calibration to Printer. Examine the RRFs and %Ds for method compliance following sections 8.6.4 through 8.6.12 of this SOP. If the continuing calibration meets QC criteria, analysis of extracts can begin.

9.2.2.2 If any of the criteria are not satisfied a second continuing calibration may be analyzed. Repeated failure requires the analysis of a new initial calibration before analysis of samples can begin. If repairs to the system are required then a new initial calibration must be performed.

9.2.2.3 Take corrective action if the continuing calibration fails. This may consist of re-analyzing the standard, clipping the column and replacing the injection port seal, or creating a new five point calibration.

9.2.3 Sample analysis.

Samples can be analyzed only after the DFTPP tune and initial calibration or continuing a calibration meet all of the appropriate criteria specified in Section 8 of this SOP.

9.2.3.1 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Appendix E.

9.2.3.2 Set up a data acquisition sequence. The sample description shall include the client sample ID and the laboratory sample ID. Additional header information shall include the dilution factor, instrument ID, and the analyst's initials.

9.2.3.3 Add 10 μL of the IS solution to each 1 mL of field and QC sample extract.

9.2.3.4 Include all QC sample extracts. It is highly recommended that the LRB, LFB and LFM/LFMD extracts be analyzed as early as possible in the analysis of a batch.

9.2.3.5 After completion of analysis, quantitate the data using the appropriate initial calibration mean RRF's and print out quantitation reports and chromatograms for each field and QC sample.

9.2.3.6 Review the results as discussed in Section 8.14 for identification of target analytes. Manually cross out all reported hits which do not meet the qualitative criteria and document the reason on the quant report. Review all target compounds that are detected to verify they are integrated properly. Review the chromatogram for possible false negatives.

9.2.3.7 Document any required manual integrations as described in Section 8.5.11 and Region 9 SOP #835. Print out the updated quantitation report.

9.2.3.8 Check the sample's internal standard area counts and surrogate recoveries with the criteria in Section 8.11 and 8.12.

9.2.3.9 Dilute and re-analyze the sample extracts if any of the target analytes exceed the calibration range of the instrument. Dilute the extract so that the most prominent target compound will fall within the upper half of the initial calibration range of the instrument.

9.3 Tentatively Identified Compounds (TICs)

9.3.1 Load the data file of the most concentrated valid analysis of the sample.

9.3.2 Examine the spectra for each peak that is not a target, surrogate or internal standard. See how well it matches the tentative identifications given by the data system. Report any unique, likely match, if there is one. If none, so state. Try to give as much information as possible, e.g., "unknown polynuclear aromatic hydrocarbon," "unknown, molecular weight 205 daltons".

9.3.3 The concentration of TIC's should be estimated. Use the TIC area in Equations 9 and 10 and assume the RRF is 1. Use the nearest internal standard free of interferences.

9.3.4 If the base peak saturates the detector, document this in the data. Do not dilute a sample extract to get the base peak of a TIC within the detector range. If a sample extract containing a saturated TIC ion was diluted to get a target compound within calibration range, use the TIC base peak area from the diluted extract to estimate the concentration of the TIC.

9.4 The following are suggested corrective actions which may improve method performance. Document all routine maintenance or corrective actions taken in the maintenance logbook.

9.4.1 Adjust the mass gain and peak width or re-calibrate the mass axis or retune the mass spectrometer.

9.4.2 Replace the injection liner and/or the inlet seal.

9.4.3 Break off a portion of the column (a few inches to a foot or more) from the injector end.

9.4.4 Prepare fresh standard solutions

9.4.5 Clean the ion source

10 DOCUMENTATION

10.1 Data from the Region 9 Laboratory is presented to the client in one of two general reporting formats: a complete data package or a summary report data package. For the former the laboratory provides summary forms of calibration, quality control, and sample results along with the raw data for standards and field and QC samples, logbook pages, a report narrative, and the analytical report spreadsheet to the client. If a summary package is all that is required the laboratory provides a report narrative, analytical results spreadsheet, and sample specific raw data for delivery to the client and collects all other data included in a complete data package and files it at the laboratory. Section 10.2 details the requirements of a complete data package and Section 10.3 lists the summary report requirements.

10.2 Assembly of a complete data package.

A data package for each SDG in each case requiring the delivery of a complete data package shall be assembled by the analyst, or other chemist, according to the following instructions, and in the following order. Each section of the data package shall have a cover sheet titled with the appropriate section name. The data package shall be sequentially numbered after assembly using a hand-operated numerator.

10.2.1 Report Narrative section.

10.2.1.1 The Report Narrative section contains a text narrative describing, but not limited to, the following.

10.2.1.1.1 Site name.

10.2.1.1.2 Case number.

10.2.1.1.3 SDG number.

10.2.1.1.4 Client sample ID - Laboratory sample ID cross reference

10.2.1.1.5 Date(s) the samples were received.

10.2.1.1.6 Protocol used to analyze the samples

10.2.1.1.7 LRB results

10.2.1.1.8 Surrogate recoveries

10.2.1.1.9 Internal standard recoveries.

10.2.1.1.10 LFM/LFMD results.

10.2.1.1.11 LFB results.

10.2.1.1.12 Analytical comments section to include:

10.2.1.1.12.1 Problems with analysis

10.2.1.1.12.2 Examples of calculations

10.2.2 Summary of Analytical Results spreadsheet

10.2.2.1 Include a spreadsheet containing a summary of the results for all target analytes for all samples and LRB's in the data package.

10.2.2.2 The header information for each sample contains the station location, Sample ID, and date sampled.

10.2.2.3 The results section contains the results for each target analyte as follows:

If an analyte is not detected then the quantitation limit with a "U" qualifier will be reported

If an analyte is detected then the value reported on the quant report and the associated qualifier (Section 10.2.5.1) will be reported.

If an analyte requires a dilution then value from the sample dilution will be reported.

10.2.3 Tracking Forms section.

The Tracking Form section contains the following forms.

10.2.3.1 A technical direction form

10.2.3.2 A copy of the chain of custody records received with each sample shipment.

10.2.3.3 A copy of the shipper's air bill, or bill of lading.

10.2.4 QA/QC Summary section.

The QA/QC section contains all of the QA/QC summary forms for the specific sample delivery group. All of the forms are checked by the analyst to ensure that all of the filenames are correct, and that all of the appropriate standards, blanks, samples and spikes have been included.

10.2.4.1 Data analysis of sample SDG matrix summary report

10.2.4.2 Surrogate recovery and internal standard area count data. In a chronological order by instrument.

10.2.4.3 LFB recovery data.

10.2.4.4 LFM and LFMD recovery data.

10.2.5 Initial Calibration section:

10.2.5.1 Copy of the peer reviewed instrument run log page(s).

10.2.5.2 DFTPP tuning report, which includes the pass/fail table, bar spectrum and tabulated mass listing.

10.2.5.3 Initial calibration summary form containing the response factors for each file, the average response factor for each compound, and the percent RSD for each compound in the initial calibration.

10.2.5.4 Quantitation reports and RICs.

10.2.5.5 Documentation of any required manual integrations as described in Section 8.5.11 and Region 9 SOP #835.

10.2.6 Daily Sample Package section.

The daily sample package section contains the following forms and raw data for each sample including QC samples of LFM/LFMD, LFB, and LRB in the data package, assembled in data file alphanumeric order. Each daily package is arranged in chronological order.

10.2.6.1 Quantitation report, data report form listing all detected target compounds, surrogates and internal standards and the levels detected in the sample. All analyses must be included, even those not used. The analyst shall check to be sure that the appropriate qualifier is added to the form as indicated below.

B This analyte was detected in the associated method blank as well as in the sample.

E The amount detected exceeds the calibration range of the instrument.

J The analyte was positively identified . The amount is less than QL but greater than or equal to ½ of QL and/or the associated numerical value is approximate. It is an estimated value.

10.2.6.2 The reconstructed ion chromatogram (RIC) of the data file.

10.2.6.3 The raw spectra and enhanced spectra of the target compounds, internal standards and surrogates detected in the sample, as well as the corresponding reference spectra in order of elution.

10.2.6.4 Documentation of any required manual integrations as described in Section 8.5.11 and Region 9 SOP #835.

10.2.6.5 Non-target compound report form detailing the compound names, retention times, the estimated concentrations, and the CAS number of up to twenty tentatively identified compounds. The exceptions are QC samples of LFB, LFM/LFMD.

10.2.6.6 Enhanced spectra of non-target compounds detected in the sample. Library search listing the three best fits of a forward library search of the non-target compounds.

10.2.6.7 Area summary showing results of integrating the RIC.

10.2.7 Logbooks and Miscellaneous Data.

All logbooks must be peer reviewed and complete in compliance with USEPA Region 9 Laboratory SOP #840, Notebook Documentation and Control.

10.2.7.1 Copies of all applicable standards preparation logbook pages.

10.2.7.2 Copies of extraction log pages.

10.2.7.3 Copies of Percent Solids logbook pages, if applicable.

10.2.7.4 Copies of GPC run log logbook pages, if applicable

10.2.7.5 Copies of applicable Semivolatile Organics Run Log pages

10.3 Summary Report and Raw Data

When the clients' requirements stipulate a summary data package, the laboratory prepares the report narrative, analytical results spreadsheet, and sample specific raw data and organizes other data associated with the package for filing in the event that future data review or validation is required.

10.3.1 Prepare the report narrative according to the requirements listed in Section 10.2.1.

10.3.2 Prepare the analytical results spreadsheet according to the specifications provided in Section 10.2.2.

10.3.3 Organize the raw data associated with the analysis of all the samples in the package for filing and present it for review along with the report narrative and the spreadsheet. No summary forms need be generated with the raw data but any forms which would normally be generated as part of the analysis must be included in the package. For example, the calibration summary reports generated by the data system and used by the analyst to assess the acceptability of the calibration should be filed with the raw data.

10.3.3.1 Include sample tracking information as detailed in Section 10.2.3 as the analyst has a copy of the information readily available.

10.3.3.2 Sample raw data organized by laboratory sample ID must include: the quantitation report; the RIC; the raw and enhanced spectra of the internal standards, surrogates and any target compounds detected in the sample, as well as the enhanced spectra of the corresponding compounds in the calibration file; and enhanced spectra of non-target compounds detected in the sample along with the library search listing the three best matches for the non-target compounds. (Sections 10.2.5.3 through 10.2.5.6)

10.3.3.3 Calibration data must include any available summary information and the quantitation reports and RICs for all initial calibrations and continuing calibrations associated with the SDG. This information must be organized by instrument and date. Additionally, any manual integration must be demonstrated by including the associated peak integration as described in Section 8.5.11.

10.3.3.4 Include raw data for QC samples. Tuning data and the associated summary used by the analyst to determine acceptability, blanks (quant report, RIC and spectra and TICs), LFM/LFMD data (quant report and RICs) should all be included in this order.

10.3.3.5 Runlogs and standard preparation logbooks need not be included in the raw data as these are already filed in an accessible manner in the laboratory.

10.4 Technical review.
Assign the data package an ESAT document control number after assembly. Each data package is reviewed by the GC Group Leader or a senior level chemist, other than the chemist who performed the analyses. All reviews are documented using the review form. After the peer review is performed, a cover letter is prepared and signed by the Group Leader. Final review of the data package is done by ESAT QA/QC Coordinator or ESAT Team Leader and the package is then paginated and submitted to EPA Region 9.

10.5 Injection logbook.
Maintain an injection logbook listing each field and QC sample injected for each instrument in accordance with ESAT SOP #840, *Notebook Documentation and Control.*

10.6 Standards' logbook
Maintain a logbook documenting the preparation of all standard solutions. Record the standard ID, preparation date, expiration date, solvent and solvent lot number used. Record the identification, supplier, lot number, concentration purity, and expiration date of the stock standard solution used. Record the aliquot weight or volume of the stock standard solution, final volume of the standard solution and the concentration of the analyte(s) in the standard. Document the calculations used in preparing the standard.

10.7 Maintenance logbook
Maintain a logbook for each instrument. Record the date, the problem and resolution, and documentation of return to control. Document all preventive or routine maintenance procedures, as well as repairs or corrective or remedial actions in accordance with ESAT SOP #840, *Notebook Documentation and Control.*

11 REFERENCES

1 EPA Method 8270C, *Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)*, Revision 3, December 1996.

2 EPA Method 525.2, *Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry*, Revision 2.0, 1995

3 EPA Region 9 SOP #125. *Disposal Procedures for Unused Aqueous Environmental Samples*

4 HP 5972A MSD Hardware Manual

5 HP EnviroQuant Chemstation User's Guide

6 HP Environmental Analysis User's Guide

7 EPA Region 9 SOP #835, *Chromatographic Integration Procedures*

8 EPA Region 9 SOP #840, *Notebook Documentation and Control*

9 EPA Method 8000B, *Determinative Chromatographic Separations*, Revision 2, December 1996.

10 EPA Region 9 SOP #805, *Refrigerator Temperature Monitoring*

11 40 CFR, Part 136, Appendix B.

12 HP 5890 Gas Chromatograph Users Manual

13 HP 6890 Gas Chromatograph Users Manual

APPENDIX A

DEVIATIONS FROM SW-846 METHOD 8270C

1. There is no requirement in the reference method for the analysis of a quality control sample (QCS), or a second source standard.

2. This SOP uses a GC column with a 0.25 μm film instead of a 1 μm film as specified in the reference method.

3. The surrogate solution used in this SOP contains 1,2-dichlorobenzene-d_4 and 2-chlorophenol-d_4, neither of which are specified by method 8270.

4. The reference method recommends a concentration of 40 ng/μL in the sample extract for each internal standard; this SOP specifies 20 ng/μL instead.

5. SW-846 method 3500B referenced by method 8270C specifies a concentration of 200 mg/L for the acid matrix spiking solution; this SOP specifies 150 mg/L.

6. The reference method does not have criteria for the chromatographic separations of anthracene/phenanthrene or benzo(a)anthracene/chrysene.

7. This SOP allows for the re-analysis of certain calibration, QC, and sample solutions if the first analysis fails QC limits. This practice is not addressed in the reference method.

8. This SOP allows for a four-point calibration for certain analytes with on column quantitation limits of 25 ng (see Appendix D). The reference method requires a five-point calibration for all analytes.

9. There is no requirement in the reference method that a quantitation ion not saturate the detector.

10. There is no requirement in the reference method for the analysis of a quantitation limit standard (QLS).

11. This SOP allows the phthalate esters to be present at levels exceeding the QL in the laboratory reagent blank; the reference method does not.

12. The LFB/LFM/LFMD acceptance criteria are predetermined and fixed; they are not updated using laboratory data as in the reference method.

13. The retention times of internal standards must be within 0.2 minute from the latest daily calibration, instead of 0.5 minutes as in the reference method.

14. The acceptance criteria for surrogates are predetermined and fixed; they are not updated using laboratory data as in the reference method.

15. There is no requirement in the reference method that the response of the largest analyte peak in a dilution be kept in the upper half of the initial calibration range.

16. There is no requirement in the reference method that all ions present in the standard mass spectra at a relative intensity of 10 percent of the most abundant ion must be present in the sample spectra.

17. There is no requirement in the reference method that ions present in the sample at greater than 10 percent abundance but not present in the standard spectra must be reviewed and accounted for by the analyst making the comparison.

18. There is no requirement in the reference method that the GC/MS system is to be checked for leaks prior to the analysis of the tuning compound by monitoring m/z's 18, 28, and 69.

19. Diphenylamine is not used as a CCC in this SOP as in the reference method since it is not a target analyte in this SOP.

20. The maximum RSD of target analytes in the initial calibration in this SOP is 20%, not 15% as in the reference method.

21. The maximum RSD for any CCC in this SOP is 20%, not 30% as in the reference method.

22. The maximum %D for any CCC in this SOP is 25, not 20 as in the reference method.

23. The reference method has no %D criteria for analytes in the calibration verification other than the calibration check compounds (CCC's).

APPENDIX B
Calibration Criteria

SEMIVOLATILE COMPOUND	MINIMUM RRF	MAXIMUM %RSD	MAXIMUM %DIFF
Phenol	0.800	20	±25
bis(2-Chloroethyl)ether	0.700	20	±25
2-Chlorophenol	0.800	20	±25
1,3-Dichlorobenzene	0.600	20	±25
1,4-Dichlorobenzene	0.500	20	±25
benzyl alcohol	0.050	20	±25
1,2-Dichlorobenzene	0.400	20	±25
2-Methylphenol	0.700	20	±25
2,2'-oxybis(1-Chloropropane)	0.010	20	±25
4-Methylphenol	0.600	20	±25
N-Nitroso-di-n-propylamine	0.050	20	±25
Hexachloroethane	0.300	20	±25
Nitrobenzene	0.200	20	±25
Isophorone	0.400	20	±25
2-Nitrophenol	0.100	20	±25
2,4-Dimethylphenol	0.200	20	±25
bis(2-Chloroethoxy)methane	0.300	20	±25
2,4-Dichlorophenol	0.200	20	±25
1,2,4-Trichlorobenzene	0.200	20	±25
Naphthalene	0.700	20	±25
4-Chloroaniline	0.010	20	±25
Hexachlorobutadiene	0.010	20	±25
4-Chloro-3-methylphenol	0.200	20	±25
2-Methylnaphthalene	0.400	20	±25
Hexachlorocyclopentadiene	0.050	20	±25
2,4,6-Trichlorophenol	0.200	20	±25
2,4,5-Trichlorophenol	0.200	20	±25
2-Chloronaphthalene	0.800	20	±25
2-Nitroaniline	0.010	20	±25
Dimethylphthalate	0.010	20	±25
Acenaphthylene	0.900	20	±25
3-Nitroaniline	0.010	20	±25
2,6-Dinitrotoluene	0.200	20	±25
Acenaphthene	0.900	20	±25
2,4-Dinitrophenol	0.050	20	±25
4-Nitrophenol	0.050	20	±25
Dibenzofuran	0.800	20	±25
2,4-Dinitrotoluene	0.200	20	±25
Diethylphthalate	0.010	20	±25
4-Chlorophenyl-phenylether	0.400	20	±25
Fluorene	0.900	20	±25
4-Nitroaniline	0.010	20	±25
4,6-Dinitro-2-methylphenol	0.010	20	±25
N-Nitrosodiphenylamine	0.010	20	±25
4-Bromophenyl-phenylether	0.100	20	±25
Hexachlorobenzene	0.100	20	±25

SEMIVOLATILE COMPOUND	MINIMUM RRF	MAXIMUM %RSD	MAXIMUM %DIFF
Pentachlorophenol	0.050	20	±25
Phenanthrene	0.700	20	±25
Anthracene	0.700	20	±25
Carbazole	0.010	20	±25
Di-n-butylphthalate	0.010	20	±25
Fluoranthene	0.600	20	±25
Pyrene	0.600	20	±25
Butylbenzylphthalate	0.010	20	±25
3,3'-Dichlorobenzidine	0.010	20	±25
Benzo(a)anthracene	0.800	20	±25
bis(2-Ethylhexyl)phthalate	0.010	20	±25
Chrysene	0.700	20	±25
Di-n-octylphthalate	0.010	20	±25
Benzo(b)fluoranthene	0.700	20	±25
Benzo(k)fluoranthene	0.700	20	±25
Benzo(a)pyrene	0.700	20	±25
Indeno(1,2,3-cd)pyrene	0.500	20	±25
Dibenzo(a,h)anthracene	0.400	20	±25
Benzo(g,h,i)perylene	0.500	20	±25
SURROGATES			
Nitrobenzene-d5	0.200	20	±25
2-Fluorobiphenyl	0.700	20	±25
Terphenyl-d14	0.500	20	±25
Phenol-d5	0.800	20	±25
2-Fluorophenol	0.600	20	±25
2,4,6-Tribromophenol	0.010	20	±25
2-Chlorophenol-d4	0.800	20	±25
1,2-Dichlorobenzene-d4	0.400	20	±25

APPENDIX C

TARGET COMPOUND LIST FOR SEMIVOLATILE ORGANICS ANALYSIS

The following is the Target Compound List for semivolatile organics, as well as the associated internal standards and surrogates. Included are the internal standard reference for each target compound, as well as the quantitation mass for each analyte.

Compound	Primary Quant Ion	Secondary Ion(s)	Int. Std
Phenol	94	65, 66	1
bis(2-Chloroethyl)ether	93	63, 95	1
2-Chlorophenol	128	64, 130	1
1,3-Dichlorobenzene	146	148, 113	1
1,4-Dichlorobenzene	146	148, 113	1
benzyl alcohol	108	79, 77	1
1,2-Dichlorobenzene	146	148, 113	1
2-Methylphenol	108	107	1
2,2'-oxybis(1-Chloropropane)	45	77, 79	1
4-Methylphenol	108	107	1
N-Nitroso-di-n-propylamine	70	42, 101, 130	1
Hexachloroethane	117	201, 199	1
Nitrobenzene	77	123, 65	2
Isophorone	82	95, 138	2
2-Nitrophenol	139	65, 109	2
2,4-Dimethylphenol	107	121, 122	2
bis(2-Chloroethoxy)methane	93	95, 123	2
2,4-Dichlorophenol	162	164, 98	2
1,2,4-Trichlorobenzene	180	182, 145	2
Naphthalene	128	129, 127	2
4-Chloroaniline	127	129	2
Hexachlorobutadiene	225	223, 227	2
4-Chloro-3-methylphenol	107	144, 142	2
2-Methylnaphthalene	142	141	2
Hexachlorocyclopentadiene	237	235, 272	3
2,4,6-Trichlorophenol	196	198, 200	3
2,4,5-Trichlorophenol	196	198, 200	3
2-Chloronaphthalene	162	164, 127	3
2-Nitroaniline	65	92, 138	3
Dimethyl phthalate	163	194, 164	3
Acenaphthylene	152	151, 153	3
2,6-Dinitrotoluene	165	89, 121	3
3-Nitroaniline	138	108, 92	3
Acenaphthene	153	152, 154	3
2,4-Dinitrophenol	184	63, 154	3
4-Nitrophenol	109	139, 65	3
Dibenzofuran	168	139	3
2,4-Dinitrotoluene	165	63, 182	3
Diethylphthalate	149	177, 150	3
4-Chlorophenyl-phenylether	204	206, 141	3
Fluorene	166	165, 167	3
4-Nitroaniline	138	92, 108	3

Compound	Primary Quant Ion	Secondary Ion(s)	Int. Std
4,6-Dinitro-2-methylphenol	198	182, 77	4
N-Nitrosodiphenylamine	169	168, 167	4
4-Bromophenyl-phenylether	248	250, 141	4
Hexachlorobenzene	284	142, 249	4
Pentachlorophenol	266	264, 268	4
Phenanthrene	178	179, 176	4
Anthracene	178	179, 176	4
Carbazole	167	166, 139	4
Di-n-butylphthalate	149	150, 104	4
Fluoranthene	202	101, 100	4
Pyrene	202	101, 100	5
Butylbenzylphthalate	149	91, 206	5
3,3'-Dichlorobenzidine	252	254, 126	5
Benzo(a)anthracene	228	229, 226	5
bis(2-Ethylhexyl)phthalate	149	167, 279	5
Chrysene	228	226, 229	5
Di-n-Octyl phthalate	149	150, 279	6
Benzo(b)fluoranthene	252	253, 125	6
Benzo(k)fluoranthene	252	253, 125	6
Benzo(a)pyrene	252	253, 125	6
Indeno(1,2,3-cd)pyrene	276	138, 227	6
Dibenzo(a,h)anthracene	278	139, 279	6
Benzo(g,h,i)perylene	276	138, 277	6
SURROGATES			
Phenol-d5	99	42, 71	1
2-Fluorophenol	112	64	1
2,4,6-Tribromophenol	330	332, 141	4
Nitrobenzene-d5	82	128, 54	2
2-Fluorobiphenyl	172	171	3
Terphenyl-d14	244	122, 212	5
2-Chlorophenol-d4	132	68, 134	1
1,2-Dichlorobenzene-d4	152	115, 150	1
INTERNAL STANDARDS			
1,4-Dichlorobenzene-d4	152	115	1
Naphthalene-d8	136	68	2
Acenaphthene-d10	164	162, 160	3
Phenanthrene-d10	188	94, 80	4
Chrysene-d12	240	120, 236	5
Perylene-d12	264	260, 265	6

APPENDIX D

SEMIVOLATILES TARGET COMPOUND LIST AND QUANTITATION LIMITS

Semivolatiles	CAS Number	Water µg/L	Low Soil µg/Kg	Med. Soil µg/Kg	On Column ng
Phenol	108-95-2	10	330	10000	10
bis-(2-Chloroethyl)ether	111-44-4	10	330	10000	10
2-Chlorophenol	95-57-8	10	330	10000	10
1,3-Dichlorobenzene	541-73-1	10	330	10000	10
1,4-Dichlorobenzene	106-46-7	10	330	10000	10
benzyl alcohol	100-51-6	10	330	10000	10
1,2-Dichlorobenzene	95-50-1	10	330	10000	10
2-Methylphenol	95-48-7	10	330	10000	10
2,2'-oxybis (1-Chloropropane)	108-60-1	10	330	10000	10
4-Methylphenol	106-44-5	10	330	10000	10
N-Nitroso-di-n-propylamine	621-64-7	10	330	10000	10
Hexachloroethane	67-72-1	10	330	10000	10
Nitrobenzene	98-95-3	10	330	10000	10
Isophorone	78-59-1	10	330	10000	10
2-Nitrophenol	88-75-5	10	330	10000	10
2,4-Dimethylphenol	105-67-9	10	330	10000	10
bis(2-Chloroethoxy)methane	111-91-1	10	330	10000	10
2,4-Dichlorophenol	120-83-2	10	330	10000	10
1,2,4-Trichlorobenzene	120-82-1	10	330	10000	10
Naphthalene	91-20-3	10	330	10000	10
4-Chloroaniline	106-47-8	10	330	10000	10
Hexachlorobutadiene	87-68-3	10	330	10000	10
4-Chloro-3-methylphenol	59-50-7	10	330	10000	10
2-Methylnaphthalene	91-57-6	10	330	10000	10
Hexachlorocyclopentadiene	77-47-4	10	330	10000	10
2,4,6-Trichlorophenol	88-06-2	10	330	10000	10
2,4,5-Trichlorophenol	95-95-4	25	830	25000	25
2-Chloronaphthalene	91-58-7	10	330	10000	10
2-Nitroaniline	88-74-4	25	830	25000	25
Dimethylphthalate	131-11-3	10	330	10000	10
Acenaphthylene	208-96-8	10	330	10000	10
2,6-Dinitrotoluene	606-20-2	10	330	10000	10
3-Nitroaniline	99-09-2	25	830	25000	25
Acenaphthene	83-32-9	10	330	10000	10
2,4-Dinitrophenol	51-28-5	25	830	25000	25
4-Nitrophenol	100-02-7	25	830	25000	25
Dibenzofuran	132-64-9	10	330	10000	10
2,4-Dinitrotoluene	121-14-2	10	330	10000	10
Diethylphthalate	84-66-2	10	330	10000	10
4-Chlorophenyl-phenylether	7005-72-3	10	330	10000	10
Fluorene	86-73-7	10	330	10000	10
4-Nitroaniline	100-01-6	25	830	25000	25
4,6-Dinitro-2-methylphenol	534-52-1	25	830	25000	25
N-Nitroso-diphenylamine	86-30-6	10	330	10000	10
4-Bromophenyl-phenylether	101-55-3	10	330	10000	10
Hexachlorobenzene	118-74-1	10	330	10000	10
Pentachlorophenol	87-86-5	25	830	25000	25

Phenanthrene	85-01-8	10	330	10000	10
Anthracene	120-12-7	10	330	10000	10
Carbazole	86-74-8	10	330	10000	10
Di-n-butylphthalate	84-74-2	10	330	10000	10
Fluoranthene	206-44-0	10	330	10000	10
Pyrene	129-00-0	10	330	10000	10
Butylbenzylphthalate	85-68-7	10	330	10000	10
3,3'-Dichlorobenzidine	91-94-1	10	330	10000	10

Semivolatiles	CAS Number	Water µg/L	Low Soil µg/Kg	Med. Soil µg/Kg	On Column (ng)
Benzo(a)anthracene	56-55-3	10	330	10000	10
Chrysene	218-01-9	10	330	10000	10
bis(2-Ethylhexyl)phthalate	117-81-7	10	330	10000	10
Di-n-octylphthalate	117-84-0	10	330	10000	10
Benzo(b)fluoranthene	205-99-2	10	330	10000	10
Benzo(k)fluoranthene	207-08-9	10	330	10000	10
Benzo(a)pyrene	50-32-8	10	330	10000	10
Indeno(1,2,3-cd)-pyrene	193-39-5	10	330	10000	10
Dibenzo(a,h)-anthracene	53-70-3	10	330	10000	10
Benzo(g,h,i)perylene	191-24-2	10	330	10000	10

APPENDIX E

GC PARAMETERS

HP6890

Typical operating parameters for the gas chromatograph are as follows:

DFTPP analysis

PARAMETER	SETTING
Injector temperature	280 C
Column Stability time	0.5 minutes
MS Source Temp	230 C
MS Quad Temp	150 C
MSD Heater Temp	280 C
EPC split-splitless inlet	Pulsed splitless
Injection pulse pressure	20 psi until 0.55 min
Purge flow to split vent	20 ml/min @ 0.50 min
Initial Oven Temp	100 C
Initial Oven Time	0 minutes
Temperature Ramp	20 C/minute for 10 minutes
Final Oven Temp	300 C
Final Hold Time	2 minutes
Column Flow rate	~ 1 mL/min
Electron Energy	70 volts (nominal)
Injector	Front
Injection Volume	1.0 µL
Pre Injection	
Sample Washes	0
Solvent A Washes	1
Solvent B Washes	0
Post Injection	
Solvent A Washes	3
Solvent B Washes	3
Pumps	3
Syringe Size	10 µL
Viscosity	0
Plunger Speed	Fast Injection

Target Compound Analysis

PARAMETER	SETTING
Injector temperature	280 C
Column Stability time	0.5 minutes
MS Source Temp	230 C
MS Quad Temp	150 C
MSD Heater Temp	280 C
EPC split-splitless inlet	Pulsed splitless
Injection pulse pressure	20 psi until 0.55 min
Purge flow to split vent	20 ml/min @ 0.50 min
Initial Oven Temp	40 C
Initial Oven Time	1 minutes
Temperature Ramp	20 C/minute
Final Oven Temp	130 C
Temperature Ramp A	12 C/minute
Final Oven Temp A	270 C
Temperature Ramp B	4 C/minute
Final Oven Temp B	313 C
Final Hold Time	2 minutes
Column Flow rate	~ 1 mL/min
Electron Energy	70 volts (nominal)
Injection Volume	1.0 μL
Pre Injection	
Sample Washes	0
Solvent A Washes	1
Solvent B Washes	0
Post Injection	
Solvent A Washes	3
Solvent B Washes	3
Pumps	3
Syringe Size	10 μL
Viscosity	0
Plunger Speed	Fast Injection

Amendment to Region 9 SOP #315

The Region 9 SOP # 315 "*SEMIVOLATILE ORGANICS ANALYSIS*" is amended to allow for the addition of 1,4-dioxane as an analyte as follow:

Initial Calibration:

The SVOC initial calibration mix was modified to include 1,4-dioxane as follow:

Level	1	2	3	4	5
SVOC IS (ng/ L)	20	20	20	20	20
SVOC Targets (ng/ L)	10	25	40	60	80
1,4-dioxane-d8 (ng/ L)	5	5	5	5	5
1,4-dioxane (ng/ L)	1	2	5	10	20

Initial results indicate that 1,4-dioxane response is linear over the above calibration range; thus, it would be reasonable to assign the normal SVOC %RSD limit of ± 20%.

1,4-Dioxane-d8 is utilized as an internal standard and as a surrogate as follow:

1,4-dioxane-d8 (internal standard): 1,4-dioxane-d8 is treated as a normal SVOC standard with the exception that it is spiked at the 5 ng/ L. Native 1,4-dioxane concentration is calculated based on 1,4-dioxane-d8.

1,4-Dioxane-d8 (surrogate): 1,4-dioxane-d8 concentration is calculated based on 1,4-dichlorobenzene-d4 (SVOC IS1).

Two entries for 1,4-dioxane-d8 will appear in the raw data. The above method allows us to determine the actual recovery of 1,4-dioxane-d8 (as a surrogate) and to correct for the extraction efficiency of native 1,4-dioxane.

Continuing Calibration:

The continuing calibration will be analyzed at level two (2 ng/ L). 1,4-Dioxane response appears to be linear; thus, it would be reasonable to assign the normal SVOC %D limit of ± 25%.

Quantitation Level Standard:

The QLS is analyzed at the 1 ng/ L level with a recovery limit of 50-150%.

Surrogate:

1,4-Dioxane-d8 is added to the SVOC surrogate mix at the 5 ng/ L level. The method blanks, blank spikes, and field samples are spiked with the surrogate during extraction. The SVOC surrogate recovery limits vary depending on the specific SVOC surrogate. Initial analysis results indicate that 1,4-dioxane-d8 was recovered in the 76-124% range in the MDL and P&A standards. For field samples, an initial surrogate recovery limit of 50-130% is therefore recommended.

Matrix Spike:

The SVOC matrix spike mix is modified to include 1,4-dioxane at the 5 g/L level. Initial analysis results indicate that 1,4-dioxane was recovered in the 72-97% range in the MDL and P&A standards. For field samples, initial MS/MSD recovery limits of 50-130% is therefore recommended.